Environmental and relative sea-level reconstruction from isolation basins in NW Scotland using geochemical techniques

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ENVIRONMENTAL AND RELATIVE SEA-LEVEL RECONSTRUCTION FROM ISOLATION BASINS IN NW SCOTLAND USING GEOCHEMICAL TECHNIQUES

Volume One:

Main Text, Tables, References and Appendices

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Declaration

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any or other university. In all cases, where it is relevant, material from the work of others has been acknowledged.

ABSTRACT

Isolation basins from Northwest Scotland provide the longest near-field records of relative sea-level (RSL) change in the world (0 to > 16kyr BP). These archives contributed to quantitative models of glacial isostatic adjustment since the last glacial maximum. Isolation basin RSL reconstructions have been primarily based on salinity reconstructions from biological data such as foraminifera and diatoms. However, preservation problems and non-analogue situations can limit their usefulness. Therefore, it is necessary to identify other proxies from isolation basin to improve RSL reconstructions. Also isolation basin sediments are potentially high-resolution records of climate change from both the land and the oceans simultaneously, but little research has been undertaken. This thesis presents the results of a range of isotopic and geochemical measurements that were thought to be suitable proxies for palaeosalinity and palaeoclimate reconstructions. Tephrochronology was also applied to improve the existing geochronological controls of isolation basin sequences by attempting to identify Icelandic tephra layers.

A combination of isotopic measurements; $\delta^{13}C_{org}$, C/N ratios $\delta^{13}C_{foram}$, $\delta^{18}O_{foram}$, $^{87}Sr/^{86}Sr$ from foraminifera and $\delta^{18}O_{diatoms}$, were preformed on contemporary and fossil archives. Results show $\delta^{13}C_{org}$, C/N ratios measurements are as sensitive indicators of palaeosalinity, as biological reconstructions on Holocene aged sediment. Overall this thesis highlights the benefits of multi proxy palaeosalinity studies in order to gain a fuller understanding of the complex changes isolation basins experience during an isolation or connection events.

A climate signal from an isolation basin that experienced a gradual isolated over the Holocene has been detected for the first time using geochemical techniques biogenic silica ($BSiO_2$) and total organic carbon (TOC).

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Environmental and relative sea-level reconstruction from isolation basins in NW Scotland using geochemical techniques

Cover image: Sun setting over the Ru Peninsula, Arisaig, Northwest Scotland looking over towards Eigg during field work August 2002.

Chapter 1

Introduction: Isolation basins and relative sea level change

1.1 Introduction

The Quaternary period has witnessed many rapid and dramatic changes in relative sea-level (RSL - the position of the sea relative to the land, influenced by the interplay between eustatic and isostatic processes) that have helped to shape the landscape of today. With the current concerns about global warming and the possible effects on global sea levels, RSL change has become an important research priority. One of the ways RSL has been studied is with the use of isolation basin sediments. Isolation basin sediments have been used to reconstruct RSL in numerous countries, for example, in Scandinavia (Fargri, 1940; Hafsten and Tallantire, 1978; Kjemperud, 1981a, 1981b; 1986; Bondevik *et al.*, 1997a, 1997b, 1998; Eronen *et al.*, 2001), Greenland (Foged, 1972; Bennike, 1995; Long *et al.*, 1999; Long *et al.*, 2003), Canada (Rettelle *et al.*, 1989) and Russia (Snyder *et al.*, 1997; Corner *et al.*, 1999, 2001). In NW Scotland over the last 20 years the isolation basin methodology has been one of the main ways that sea-level has been reconstructed (e.g. Dickson *et al.*, 1978; Thompson and Wain-Hobson, 1979; Shennan *et al.*, 1993, 1994, 1995, 1996a, 1996b, 1999, 2000; Lloyd, 2000; Lloyd and Evans, 2002).

Isolation basins and RSL reconstruction

An isolation basin is a natural rock depression that may, at various times in its history, be connected to or isolated from the sea by changes in RSL (Long *et al.*, 1999). An isolation basin is morphologically different from a coastal lagoon.

Isolation basins have rock sills (the lowest point between the basin and the open sea) making them impermeable to seawater seepage; in contrast coastal lagoons commonly have a sand or gravel barrier, which makes them susceptible to seawater percolation, creating more complex records of RSL. Figure 1.1 shows a schematic model of an isolation basin during a RSL fall, during which the environment of the isolation basin alters from fully marine (Stage 1), to brackish (Stages 2-3) and finally to a fully freshwater environment (Stage 4). During Stage 1 the basin is connected to the sea at all times during the tidal cycle and the water column is fully mixed. During the brackish phase (Stages 2 – 3) the basin is periodically connected to the sea allowing a mix of fresh and marine water to develop within the basin. During this stage the basin may become stratified (Kjemperud, 1986), causing a halocline to develop due to the difference in salinity between the denser marine water being overlain by a cap of less dense freshwater. By Stage 4, the altitude of the sill is higher than the level of highest astronomical tide (HAT) and therefore the basin has become completely isolated from marine inundation. At this stage a freshwater basin might be seasonally temperature-stratified depending on the depth of the lake and climatic regime of the area. Changes in RSL are preserved within the sedimentary and biological archive of isolation basins (Figures 1.2, 1.3). Typically, isolation basins can be characterised by three phases: marine, brackish and fresh. Figure 1.2 illustrates the major changes in hydrology and sediment types during a RSL fall. Figure 1.3 illustrates the range of biological assemblages and typical sediment facies deposited during the four stages associated with a RSL fall.

Following the earlier work on Scandinavian isolation basins (Hafsten and Tallanantire, 1978; Kjemperud, 1981a, 1986) a multi-proxy approach (biostratigraphic data such as foraminifera, diatoms, pollen, dinoflagellate cyst and thecamoebians; lithostratigraphic; and chronostratigraphic data via AMS and conventional radiocarbon dating) was developed to reconstruct past Scottish RSL fluctuations by determining changes in tidal inundation across the rock sill of isolation basins (Shennan *et al.,* 1993; 1994; 1995; 1996a; 1999, 2000; Lloyd, 2000). This multi-proxy approach is combined with the "sea-level tendency" methodology developed by Shennan (1982). The "sea-level tendency" methodology ascribes an *indicative meaning* to each sea level index point (i.e. a sea-level index point which shows the vertical movement of RSL identified by lithostratigraphical, micropalaeontological analysis, and radiocarbon dating), so that they can be accurately compared to one another. The *indicative meaning* is defined as the vertical relationship between the local environment in which a sea-level indicator accumulated and its contemporaneous reference tide level, for example mean high water / low water spring tide (MHWST / MLWST) (Horton *et al.,* 1999; Shennan, 1982, 1986; van de Plashe, 1986; Horton *et al.,* 1999). Each index point is ascribed an indicative range (modern vertical range occupied by the sea-level indicator) and tendency (the direction of change in water level from an increase to a decrease in marine influence; Shennan, 1982). In isolation basins the indicative meaning is not based upon the altitude of the sample itself, but the elevation of the sill. This biological approach has resulted in the development of a RSL curve for the Arisaig region by examining a series of isolation basins, at different altitudes, in the area from +0.27 m OD to +36.5 m OD, the lowest fossil isolation basin is at +4.8 m OD (Shennan *et al.,* 2000). The data show that RSL fell throughout the Lateglacial and the Younger Dryas into the early Holocene, reaching a minimum at *c.* 11.7 ka cal yrs BP (Figure 1.4). RSL rose to a mid Holocene peak of 6.5 m above present culminating at *c.* 8.0-5.0 ka cal yrs BP before falling to present (Figure 1.4). Isolation basins from NW Scotland provide one of the longest near-field records of RSL change in Britain and in the world (0 to > 16 ka cal BP, Figure 1.4, Shennan *et al.,* 2000). These archives have contributed to quantitative models of glacial isostatic adjustment and the timing and rates of global melt-water discharge since the LGM (Lambeck *et al.,* 1996; Peltier, 1998; Shennan *et al.,* 2002).

Geochemical approaches to RSL reconstruction

Despite the advances in RSL reconstruction achieved through the use of microfossils, the biological approach from isolation basins has a number of drawbacks. For example, biological indicators are not only controlled by the degree of tidal inundation controlling the salinity of the water in the basin, but also by a range of other variables such as pH, particle size, dissolved oxygen content, nutrient and organic content (Seppä *et al.*, 2000; Laidler, 2002). A geochemical investigation has shown that changes in the concentrations of certain chemical nutrients (e.g. sulphate-sulphur and sodium) can affect diatom assemblage during isolation (Seppä *et al.*, 2000). The occurrence of the diatom *Fragilaria* spp. is influenced by increases in sulphate-sulphur and sodium during and after isolation (Seppä *et al.*, 2000). Laidler (2002) suggests that the present day foraminiferal distribution in Scottish isolation basins is affected by environmental factors other than just salinity such as, pH, particle size and organic content. Combined with the problems of variable fossil abundance and preservation and non-analogue situations, there is a need to identify alternative proxies for palaeosalinity reconstruction in order to improve and extend RSL reconstructions from sites with poor microfossil preservation. The development of alternative methods for RSL reconstruction will allow a multiproxy approach to be followed. Multiproxy RSL reconstructions will highlight uncertainties and errors of single proxy reconstructions, allowing greater confidence in conclusions, which is important when attempting to model RSL change. Therefore, finding an alternative geochemical salinity proxy warrants further investigation. A number of potential geochemical proxies could be used, for example, carbon isotope ratios ($\delta^{13}C_{org}$) and carbon and nitrogen ratios (C/N), carbon and oxygen isotopes from calcareous foraminifera shells, ($\delta^{13}C_{foram}$ and $\delta^{18}O_{foram}$), oxygen isotope ratios from siliceous diatoms ($\delta^{18}O_{diatom}$), strontium isotope ratios ($^{87}Sr/^{86}Sr$) and major, minor and rare earth elements (REE) from bulk sediments.

Isolation basins as palaeoenvironmental archives

Much of the research involving isolation basins concentrates on sea-level reconstruction but isolation basins also represent significant sediment sinks, and are potentially high-resolution archives of other parameters of environmental change, such as climate change. As isolation basins are marginal marine environments, they provide a crucial link between the terrestrial and marine realms and may provide an insight into their interactions. A few studies have tried to explore this potential, for example, pollen analysis was carried out from Loch Cill Chriosd, Isle of Skye to determine the vegetation history of the area (Birks, 1973). The Holocene palaeomagnetic record was investigated from Loch Lomond and Loch Shiel, NW Scotland as a chronological tool (Dickson *et al.*, 1978; Thompson and Wain-Hobson, 1979) while Shennan *et al.* (1996b) determined the movement of the marine Polar Front during the Lateglacial based on dinoflagellate cysts from a series of basins in NW Scotland. Nevertheless, the potential of isolation basins as records of palaeoenvironmental change other than RSL has been relatively understudied. A number of international scientific programmes have been developed to understand the linkages between land-ocean interactions such as the INQUA INTIMATE project (INTegration of Ice-core, Marine and Terrestrial records) and the new International Geological Correlation Programme (IGCP) (2004-2009) project "Land-Ocean Interactions: Driving Mechanisms and Coastal Responses". There is a clear need, therefore, to examine the usefulness of isolation basin sediments as archives of palaeoclimate change. There is a great potential for the geochemical proxies biogenic silica ($BSiO_2$) and total organic carbon (TOC), as palaeoenvironmental indicators within isolation basins. $BSiO_2$ and TOC provide a means of reconstructing aquatic and terrestrial productivity signals which have been shown to be linked directly to palaeoclimate change (Conley, 1988; Schindler *et al.*, 1990).

Geochronology of isolation basin RSL curves

The RSL curves of NW Scotland have been constructed by Accelerator Mass Spectrometry carbon 14 measurements (AMS ^{14}C) dating isolation contacts (Shennan *et al.,* 2000). However, there are a number of errors / problems associated with radiocarbon dating such as; mineral carbon errors (in wash of older carbon into a sequence); plateau effects (periods of constant ^{14}C flux over time) (Lowe, 1991; Lowe and Walker, 2000; Björck *et al.,* 1996; Wohlfarth, 1996) and 'marine reservoir age' (radiocarbon age of carbon circulating in the marine system) in foraminifera (Austin *et al.,* 1995). It is unclear if isolation basin sediments need to be corrected for 'marine reservoir age' and the magnitude of any possible correction. These problems suggest that the radiocarbon dated RSL curves for NW Scotland only provide an approximate indicator of actual rate of environmental change. The problems also reduce our ability to cross-correlate RSL (and potentially palaeoclimate data) with other palaeoenvironmental records in the North Atlantic region. There is a need for an independent means of testing this AMS ^{14}C based chronology. One way of addressing this problem would be to use tephrochronology (volcanic ash layers). Tephrochronology provides the basis for time-stratigraphic markers over large distances (e.g. Lowe and Turney, 1997). Therefore, tephrochronology will not only provide a means of independently testing the AMS ^{14}C RSL curves from Northwest Scotland, it will enable correlations between RSL curves in the region and also correlation of RSL reconstructions against palaeoenvironmental records from terrestrial, ice-core and marine archives across the North Atlantic region.

1.2. Aims

This thesis aims to advance isolation basin research in 3 main ways:

1. Investigate possible geochemical means of reconstructing palaeosalinity, in order to provide alternative methods of reconstructing RSL from isolation basin sediments. This is the primary aim of the thesis.

2. Investigate further the usefulness of isolation basins as records of palaeoclimate change by using the proxies $BSiO_2$ and TOC.

3. Improve the existing geochronological controls of isolation basin sequences by attempting to identify tephra layers within isolation basin sediments.

In order to achieve these aims the following objectives were established;

1. Test a range of potential geochemical proxies $\delta^{13}C_{org}$, C/N, $\delta^{13}C_{foram}$ and $\delta^{18}O_{foram}$, $\delta^{18}O_{diatom}$, $^{87}Sr/^{86}Sr$ and major, minor and rare earth elements (REE) from sequentially leached bulk sediment, that could be applied to Scottish isolation basin sediments as palaeosalinity indicators. This will be achieved by a series of pilot studies in order to determine which proxies warranted further investigations in larger scale studies.

2. Investigate in more detail the most promising geochemical techniques identified in the pilot studies.

3. Compare $BSiO_2$ and TOC profiles against biological salinity RSL reconstructions and records of palaeoclimate change (e.g. Greenland GRIP ice core), in order to determine the controlling environmental variable upon the $BSiO_2$ and TOC from isolation basin sediments.

4. Identify if micro tephra horizons exist within isolation basin sediments from Northwest Scotland.

A range of contemporary (i.e. those with an intertidal sill) and fossil isolation basins (i.e. those with a sill above HAT, the basin may be completely infilled with sediment or where a shallow freshwater loch may remain at the site) from Arisaig, Kintail and Knapdale, NW Scotland, were chosen to test the aims and objectives of this thesis.

1.3. Thesis structure

Chapter 2 describes the background to the proxies applied, geochemical systematics and the rationale for applying each proxy to isolation basin research. Chapter 3 is a description of the field areas and individual sites across Northwest Scotland and the rationale behind the types of proxies applied to each field site. Chapter 4 details the precise methodology of each proxy used in the thesis. Chapter 5 presents the results of the pilot studies and tephra analysis. Within Chapters 6 to 8 the results of the geochemical proxies that are most suitable for palaeosalinity reconstruction within isolation basins, are discussed. Chapter 9 examines the potential for $BSiO_2$ and TOC as palaeoclimate indicators within isolation basin sediments. Chapter 10 is an assessment of the geochemical proxies compared against each other as palaeosalinity indicators. Finally, Chapter 11 will summarise the conclusions and recommend possible applications of the research findings.

Chapter 2

Review of geochemical proxies to palaeosalinity, palaeoclimate and geochronological reconstruction

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2.1 Introduction

The primary aim of this thesis is to identify alternative chemical and isotope proxies to reconstruct salinity trends within isolation basins because biological indicators suffer from variable fossil abundance, preservation and non-analogue situations. In addition biological indicators are influenced by environmental variables other than salinity such as pH, particle size, dissolved oxygen content, nutrient and organic content (Seppä *et al.*, 2000; Laidler, 2002). The secondary aim of this thesis is to identify additional records of palaeoenvironmental change other than palaeosalinity from isolation basins and improve the chronology of the existing radiocarbon dated RSL curve for NW Scotland by applying tephrochronology. This chapter presents the systematics and background rationale behind the choice of a range of potential geochemical proxies that could be applied to isolation basin sediments as palaeosalinity, palaeoclimate and geochronological indicators.

2.2 The range of techniques

A wide range of geochemical and isotope techniques are available that have the potential to reconstruct palaeosalinity and palaeoclimate. Five combinations of proxies were chosen that might potentially reconstruct salinity: carbon isotope ratios of bulk organic material ($\delta^{13}C_{org}$); carbon and nitrogen ratios (C/N) of bulk organic material; carbon and oxygen isotopes from calcareous foraminifera shells ($\delta^{13}C_{foram}$

and $\delta^{18}O_{foram}$); oxygen isotope ratios from siliceous diatoms ($\delta^{18}O_{diatom}$); strontium isotope ratios from foraminifera shells ($^{87}Sr/^{86}Sr$) and major, trace and rare earth elements (REE) from sequentially leached bulk sediments. The underlying rationale behind the choice of these particular proxies is that all of them have previously been employed with various degrees of success (with the exception of $\delta^{18}O_{diatom}$) as palaeosalinity indicators in other types of marginal environments such as estuaries, shallow shelf seas or coastal lagoons (Thornton and McManus, 1994; Chivas *et al.*, 2001; Lloyd and Evans, 2002; Reinhardt *et al.*, 1998a,b; Sternberg *et al.*, 2000). The relatively new technique of diatom oxygen isotope analysis was applied as a new method that might capture changes in the marine –freshwater environment and thought particularly useful when foraminifera are absent (Leng *et al.*, 2001). In addition, changes in the concentration of biogenic silica (%$BSiO_2$) and total organic carbon (TOC) were analysed to investigate other palaeoenvironmental signals from isolation basin sediments. Finally, tephrochronology was used to try and improve the chronology of the existing RSL curve for Northwest Scotland.

2.3 Research approach

All the isotope techniques ($\delta^{13}C_{org}$ and C/N ratios, $\delta^{18}O_{foram}$, $\delta^{13}C_{foram}$, $\delta^{18}O_{diatom}$ and $^{86}Sr/^{87}Sr$), examined as alternative methods for reconstructing salinity indirectly, will be tested in a similar way. The contemporary environment (i.e. marine, brackish and freshwater isolation basins) will be characterised and compared to results from fossil cores varying in age from the Lateglacial to the late Holocene. A range of sediment ages will be examined. This is because it is unknown if Lateglacial freshwater and marine isolation basin sediments can be isotopically distinguished from one another given that there are possibly other more significant environmental changes other than salinity, such as temperature between the Lateglacial and Holocene isolation basin sediments.

2.4 Stable isotope techniques

The seminal work of Urey (1947, 1948), combined with the instrumental standardising techniques of Craig (1953, 1957, 1961a, 1961b), developed the basis for stable isotope research. Stable isotopes are now regarded as standard proxies in many palaeoenvironmental studies and from many other materials. Examples of the wide range of palaeoenvironmental studies include oceanography (Emiliani, 1955; Shackleton, 1987), lakes (Anderson *et al.*, 2001; Saucer *et al.*, 2001) ice core studies (Johnsen *et al.*, 1972), speleothems (McDermott *et al.*, 2001), tree-rings (McCarroll and Loader, 2004), bone collagen (Stevens and Hedges, 2004) groundwaters (Rozanski, 1985; Darling *et al.*, 2003). In addition stable isotopes are also commonly used in hydrology and pollution studies (Wang *et al.*, 1999; Thornton and McManus, 1994), and biogenic silica (Labeyrie, 1974; Brandriss *et al.*, 1998; Shemesh *et al.*, 2001). Indeed, stable isotopes are now amongst the most widely used proxies in palaeoenvironmental research.

An isotope is an element that can exist in one or more stable form, due to the different number of neutrons contained within the atom. Isotopes are described as stable or radiogenic depending on whether they decay to other elements with time. Radiogenic isotopes are produced by the radioactive decay of a parent material composed of unstable elements. Stable isotope ratios are produced by "fractionation" of non-radioactive nuclides. There are over 300 stable isotopes that naturally exist (Anderson and Arthur, 1983). Carbon, oxygen, hydrogen, nitrogen and sulphur all have stable isotopes that occur in high abundance and play a key role in biological processes. Several isotopes of an element can exist for example, there are three stable isotopes of oxygen: ^{16}O, ^{17}O and ^{18}O with relative abundance in nature of 99.76%, 0.04% and 0.20%, respectively. Stable isotopes are composed of light (i.e. ^{12}C, ^{16}O) and heavy isotopes (i.e. ^{13}C, ^{18}O). Fractionation is the separation of the two isotopes into two distinct parts that have different ratios of heavy and light isotopes from the original naturally occurring ratio. Fractionation either occurs under equilibrium (themodynamic), or nonequilibrium (kinetic) conditions. Equilibrium isotope fraction involves the partitioning of isotopes between phases that are in equilibrium which are essentially temperature dependant. Nonequilibrium fractionation is the common process by which environmental isotopes (i.e. H, C, N, O and S) are separated. Nonequilibrium fractionation is the result of an irreversible physical or chemical process such as evaporation or photosynthesis. Nonequilibrium fractionation causes the lighter isotope to be preferentially removed because it has higher energy levels and therefore is more easily separated.

The degree of fractionation of stable isotope ratios is expressed by the "delta" notation (δ). Stable isotope ratios are expressed as a part per thousand or per mil (‰) deviations from a standard reference material, as defined by the equation (1):

$$\delta = [(R_{sample}) - (R_{standard})]/ (R_{standard}) \times 1000 \qquad (1)$$

(R = ratio of the heavy isotope to the light one e.g. $^{13}C/^{12}C$)

The two ratios are multiplied by 1000 to convert δ-values into per mill (‰)

There are two internationally accepted standards used to report variations in carbon and oxygen ratios: PDB (Pee Dee Belemnite) and SMOW (Standard Mean Ocean Water). PDB is a Cretaceous belemnite marine limestone from the Peedee formation in South Carolina, USA, and the scale is used for low temperature carbonates (Craig, 1957). The $\delta^{13}C$ value for PDB is defined as 0‰ and its $^{13}C/^{12}C$ ratio is 0.0112372 (Craig, 1957). The original supply of PDB, the primary standard, is now exhausted, and so measurements are now calibrated relative to the secondary standards such as NBS-20 and NBS-19 (Natural Bureau of Standards). SMOW is a hypothetical water sample with O and H isotope ratio similar to average ocean water. It is used for high temperature materials and diatom silica. The $\delta^{18}O$ value for SMOW is defined as 0‰ (Craig, 1957). A sample is described as "heavy", "higher", "enriched" or "more positive" when the sample has a δ value above the standard. A sample is described as "light", "lower", "depleted" and "more negative" when the sample has a δ value below the standard.

2.5 Organic carbon isotopes and carbon/nitrogen ratios

2.5.1 Introduction

Typically, $\delta^{13}C_{org}$ and C/N ratios are used in combination to identify the sources and the composition of sedimentary organic matter (e.g. Thornton and McManus, 1994; Yamamuro, 2000; Chivas *et al.*, 2001). These two methods will be used in tandem to identify the source of organic material preserved within isolation basin sediment.

2.5.2 Systematics and background

Stable organic carbon isotopes

The carbon isotope composition of plant matter is highly variable. Wickman (1952) and Craig (1953) were the first to demonstrate that marine organic matter has a $\delta^{13}C$ value higher than terrestrial organic matter. This difference is due to the range of organic sources from which marine and freshwater plants assimilate their carbon (Figure 2.1). Marine plants take up carbon from the total dissolved inorganic carbon pool (TDIC = HCO_3^-, CO_2^{3-} and dissolved CO_2). Marine bulk sediment $\delta^{13}C_{org}$ values range from –22‰ to –19‰ (Fontugne and Jouanneau, 1987) and marine plankton range from –22‰ to –20‰ (Gearing *et al.*, 1984). In contrast, freshwater plants predominately utilise carbon from atmospheric CO_2 which is enriched in the lighter isotope ^{12}C (Salomons and Mook, 1981; Boutton, 1991). Typically, terrestrial and freshwater aquatic plants average around –27‰ (Boutton, 1991), although freshwater plankton values range from –30‰ to –25‰ (Meyers, 1994).

Aquatic plants $\delta^{13}C$

An overlap can occur between marine and freshwater environments due to the large range of $\delta^{13}C_{org}$ displayed by freshwater aquatic plants, ranging from –50‰ to –10‰ (Keeley and Sandquist, 1992; Osmond *et al.*, 1981). Average $\delta^{13}C_{org}$ of freshwater surface sediments have a $\delta^{13}C_{org}$ composition ranging from to –31‰ to –23‰ (Filley *et al.*, 2001). The range in values occurs because aquatic plants mainly utilise either atmospheric CO_2 or carbon from the bicarbonate ion (i.e. HCO_3^-) in the

TDIC (Bain and Proctor, 1980). This depends upon the plant species, pH of the water, water turbulence and total carbon levels (Allen and Spence, 1981; Keeley and Sandquist, 1992). For example, the amount of total carbon available as CO_2 is approximately 80% at pH 5.5 compared to less than 1% at pH 8.4 (Osmond *et al.*, 1981). Aquatic plants experience additional isotopic discrimination due to the presence of 'unstirred boundary layers'. This is a layer of solution at the leaf cell surface between 10 and 500 μm thick. The thickness of the layer is dependent upon the size of the leaf and the velocity of the water (Smith and Walker, 1980). This layer causes diffusive resistance to CO_2. The diffusion of CO_2 (or HCO_3^-) in water is 10^4 times less than in air. The presence of an unstirred layer is an important rate-limiter to photosynthesis and will affect the $\delta^{13}C_{org}$ value.

In addition, the presence of limestone deposits in a catchment affects the $\delta^{13}C$ value of the TDIC in marine the aquatic environments (Fritz *et al.*, 1978). Typically, $\delta^{13}C$ values of TDIC in limestone areas have higher $\delta^{13}C$ values around –3‰ to +3‰ (Andrews *et al.*, 1997; Hudson, 1977; Fritz *et al.*, 1978). Aquatic plants in marine limestone catchment area will have significantly higher $\delta^{13}C_{org}$ values than non-limestone areas. For example, a freshwater basin dominated by decomposing terrestrial or aquatic plants (excluding salt marsh plants) that respire atmospheric CO_2 will have a TDIC pool around –27‰ (Osmond *et al.*, 1981).

Terrestrial plants

Terrestrial plants are divided into three major categories based on their metabolic pathway (Bender, 1968; Smith and Epstein, 1971), as described below,

1. Terrestrial C3 plants (such as; wheat, maple, sunflower, some grasses) have values ranging from –32‰ to –20‰, but typically around –27‰ (Boutton, 1991)
2. C4 plants (such as; sorghum, sugar, maize and some salt marsh plants e.g. *Spartina alterniflora*) have $\delta^{13}C_{org}$ values which range from –15‰ to –12‰, but are typically around –13‰ (O'Leary, 1988).

3. CAM (Crassulacean Acid Metabolism) plants are typically desert plants (e.g. *Euphorbiaceae*). CAM plants display values between –20‰ and –10‰ (Boutton, 1991).

This difference is caused by variations in carbonylating enzymes that are responsible for CO_2 fixation. C3 plants are described as "higher plants" that use a Clavin cycle pathway and use the ribulose-1, 5- biosphosphate (RuBP) carboxylase enzyme. C4 plants use the Hatch-Slack cycle utilising the phosphoenolpyruvate (PEP) carboxylase enzyme (Fry and Sherr, 1984).

The majority of the plants in the field areas in this study are C3, however salt marshes also support C4 plants (Fry and Sherr, 1984; Chmura and Aharon, 1995). C4 plants are unlikely to form a dominant component of isolation basin sediments because they only form a small part of salt marsh taxa. The prevalence of C4 plants will only ever be observed in isolation basin sediment if $\delta^{13}C_{org}$ values are high, around –14‰, accompanied by high C/N ratios of >20 (O'Leary, 1988; Meyers, 1994). The addition of C/N ratios will play an important part in identifying the contribution of C4 plants. As CAM plants only occur in deserts and tropical environments it is assumed that they do not occur around the catchment of Scottish isolation basin sediments. Overall, the $\delta^{13}C_{org}$ signal from Scottish isolation basin sediments will depend not only on the sources of aquatic organic material (marine versus freshwater) but also variations in the proportion of aquatic macrophytes to phytoplankton (see Figure 2.1) and in-wash of terrestrial material (potentially both C3 and C4).

Carbon and Nitrogen ratios

C/N ratios provide a second way of discriminating the source of organic material and are often used as an indication of the relative proportions of autochthonous and allochthonous sources of organic matter (e.g. Thornton and McManus, 1994; Yamamuro, 2000; Qiu *et al.*, 1993; Silliman *et al.*, 1996). The carbon isotope signatures of C3 terrestrial plants are similar to many freshwater algae (i.e. around

–27‰) and therefore cannot be recognized isotopically. However, C/N ratios can distinguish between aquatic and terrestrial sources of organic matter. Aquatic vegetation (including both marine and freshwater plankton) predominantly has C/N ratios of 4 – 10; submergent and floating aquatic macrophytes or a mixed source (i.e. aquatics and terrestrial plants) have ratios between 10 and 20 (Lamb *et al.*, 2004). Although some marginal macrophytes have intermediate ratios, terrestrial plants and rooted emergent vegetation generally have ratios of > 20 (Meyers, 1994; Meyers and Ishiwatari, 1993; Hassan *et al.*, 1997; Lamb *et al.*, 2004). The distinction arises because terrestrial plants are lignin and cellulose-rich and therefore contain proportionally more carbon, whereas aquatic plants are protein-rich and lack cellulosic supportive structure and therefore, have higher nitrogen levels (Meyers, 1994; Meyers and Teranes, 2001).

It is expected that marine sediment from isolation basins will be dominated by isotopically high values (–22‰ to –17‰) and low C/N ratio (<12) compared to freshwater sediment. Intermediate $\delta^{13}C_{org}$ values are expected in the brackish sections caused by the mix of marine freshwater and terrestrial organics (Gearing, 1988). Between marine and freshwater end-member environments, $\delta^{13}C_{org}$ values will be around 8‰ lower and higher C/N ratios will be >10 in freshwater sediment.

Diagenetic alterations of $\delta^{13}C_{org}$ and C/N ratios

It has been estimated that only a few percent of total organic matter escapes remineralization and destruction before permanent burial in sediment (Suess, 1980; Eadie *et al.*, 1984). Diagenesis can potentially alter $\delta^{13}C_{org}$ and C/N ratios through selective degradation of organic matter components. However, modification by diagenesis for $\delta^{13}C_{org}$ is typically very small, for example, <–2‰ even on sediment that is 91 Ma years (Hayes *et al.*, 1989; Meyer, 1994). Modification is caused by the selective loss of isotopically heavy carbohydrate compounds (e.g. cellulose) from the total organic matter (Spiker and Hatcher, 1984). A similar shift (around 1 to 2‰) in $\delta^{13}C$ ratios have been reported for degrading wood samples and were attributed to the preferential loss of cellulose relative to lignin (Spiker and Hatcher, 1987). This type of alteration typically occurs when organic matter concentrations are >20%. The organic content of limnic sediment from isolation basin sediments typically range from 10 to 20%; therefore it is possible that limnic sediment from isolation basin could suffer from diagenetic alteration. However, if the sediment has a low organic content (<3%) the sediment is not believed to be significantly affected by diagenetic alteration (Meyers and Ishiwatari, 1993). For example, in Lake Michigan, organic concentrations ranged between 1-3%, the $\delta^{13}C_{org}$ values remained at –26‰, over the last 3500 yrs suggesting digenesis did not effect $\delta^{13}C_{org}$ values of the sediment (Rae *et al.*, 1980). Isolation basin, marine sediments typically have low organic (2-3%) concentrations and therefore should not be diagenetic alteration. However, even the most extreme shift (<–2‰ shift) is unlikely to mask the difference between fully marine and freshwater $\delta^{13}C_{org}$ values which is around 8‰ (Figure 2.1).

C/N ratios are more susceptible to diagenetic change than $\delta^{13}C_{org}$. A number of estuarine studies which have used C/N ratios as a proxy to trace organic matter have found samples were diagenetically altered. For example, C/N ratios taken from the Forth and the Tay Estuaries had elevated C/N ratios when the $\delta^{13}C_{org}$ values implied the samples should have lower C/N ratios (Thornton and McManus, 1994; Graham *et al.*, 2001). In the Tay Estuary samples taken from the head of the estuary had $\delta^{13}C_{org}$ values of around –26‰ and C/N ratios between 10 and 13, while samples taken nearer the mouth of the estuary have a $\delta^{13}C_{org}$ value of –24.5‰ and –23.2‰ but C/N ratios of 15.7 and 11.3 respectively. Lower C/N ratio would typically be expected (i.e. < 10) as the $\delta^{13}C_{org}$ suggest the possible influence of marine aquatics. A number of processes can affect C/N ratios such as, selective degradation of plant compounds (e.g. proteins, lipids, carbohydrates and cellulose) and changes in particle size. Carbon-rich sugars and lipids can break down to reduce the overall C/N ratio in a terrestrial plant. For example, fresh wood has a C/N ratio of 30 but after burial the C/N ratio has reduced to 15 (Meyer *et al.*, 1995). In algae, ratios become elevated when nitrogen-rich proteins are degraded; this typically occurs in eutrophic environments (Meyers and Teranes, 2001). Changes in grain size can also influence C/N ratios, for example a coarser grain size preserves more intact plant debris and therefore it can have higher C/N ratios. Fine grained sediment can have lower C/N ratios because clay association with ammonia, which causes the uptake of inorganic nitrogen, results in the depression of C/N ratios. However, the amount of inorganic nitrogen is typically small compared to organic nitrogen in most sediments, although, if the organic content of the sediment is low, <0.3%, the proportion of inorganic nitrogen can be large (Meyer and Teranes, 2001). This suggests marine sediment could be affected by elevated C/N ratios that are controlled by inorganic nitrogen from clays. In isolation basin sediments where plant types have a large range in C/N ratios for example between algae and land plants, the magnitude of diagenesis cannot completely erase the original signal. This has been demonstrated in sediments from Lake Karewa, India, where the sediment ranges in age from 2.4 Ma to 400 ka but still the C/N ratios are still able to distinguish between terrestrial and phytoplankton sources of organic matter (Krishnamurthy *et al.*, 1986). In addition, both Chivas *et al.* (2001) and Jasper and Gasosian (1989) have found that $\delta^{13}C_{org}$ and C/N ratios record changes in the proportion of land-derived and marine organic matter over 100 ka yrs from the Gulf of Carpentaria, and the Gulf of Mexico.

2.5.3 Rationale

The rationale behind using $\delta^{13}C_{org}$ and C/N ratios is that marine sediments should record a distinctive isotopic signature compared to freshwater sediments, as shown by a number of studies in a range of marginal marine environments as tracers of organic matter and salinity. For example, $\delta^{13}C_{org}$ and C/N ratios were applied to the Tay and Forth Estuary, Scotland (Thornton and McManus, 1994; Graham *et al.*, 2001) and $\delta^{13}C_{org}$ values showed a progressive increase with salinity towards the mouth of the estuary. $\delta^{13}C_{org}$ values in the Tay Estuary increased from 26.6‰ to 23.2‰, from the head to just before the mouth of the estuary (Thornton and McManus, 1994). However, as noted above the C/N signal in both estuaries was found to be over-printed by diagenetic processes. In Japan, Yamamuro (2000) also found that $\delta^{13}C_{org}$ values increased with salinity in two coastal lagoons. C/N ratios provided additional information as to the origin of the organic matter in the sediments. The proxies have also been successfully used to characterise the salinity of salt marsh deposits in the Mississippi Delta (Chmura and Aharon 1995), Humber Estuary (Andrews *et al.*, 2000) and San Francisco Estuary (Byrne *et al.*, 2001). For example, Byrne *et al.* (2001) used $\delta^{13}C_{org}$ to detect four periods of relatively high and low salinity associated with human activities and changes in the climate influencing the freshwater inflow to the brackish marshes in San Francisco Estuary during the late Holocene. The techniques have also been used to characterise trends in palaeosalinity associated with RSL change from shallow sea sediments. Examples include the last interglacial sediment of the Gulf of Carpentaria (<100 m deep), Australia (Chivas *et al.*, 2001) and the Lateglacial and Holocene sediments of the Baltic sea (Müller and Voss, 1999; Westman and Hedenström, 2002; Emeis *et al.*, 2003). Only one study is known to have previously used $\delta^{13}C_{org}$ and C/N ratios on isolation basin sediments of comparable size to Scottish isolation basins to be examined in this study. Vorren *et al.* (1988) used the $\delta^{13}C_{org}$ and C/N results provided as part of radiocarbon analysis in a Lateglacial isolation boundary in Andøya, northern Norway. The lowest $\delta^{13}C_{org}$ values (–25‰ to –30‰) were found from the marine section of the core while values as high as –15‰ to –14‰ were measured from freshwater sediment. Climatic effects were suggested as the cause for the shift from the expected values. Similar offsets have been recorded in Lateglacial and Younger Dryas freshwater sediments across Europe, for example, lacustrine records in southern Sweden (Hammarlund and Lemdahl, 1993) and across Scotland, England and Wales (Turney, 1999; Nuñez *et al.*, 2001; Walker *et al.*, 2003); all report a shift from isotopically higher to lower values across the Lateglacial/early Holocene transition reflecting the influence of palaeoclimate on the $\delta^{13}C_{org}$ values. For example an infilled kettle-hole at Llanilid, south Wales records a $\delta^{13}C_{org}$ shift across Younger Dryas sediment of around 4‰ (Turney, 1999; Walker *et al.*, 2003).

2.5.4 Summary

Despite the possible influence of palaeoclimate effects on the salinity signals and problems associated with aquatic plant $\delta^{13}C_{org}$ values (Sandhurst and Keely, 1992), $\delta^{13}C_{org}$ and C/N ratios are likely to be ideal palaeosalinity proxies for Scottish isolation basin sediments for several key reasons;

1. $\delta^{13}C_{org}$ and C/N ratios are measured on the same bulk sediment and have the potential to reconstruct salinity trends in sites devoid of microfossil or with poor microfossil preservation.

2. All stages of the isolation process can be reconstructed, which is not possible when using carbonate proxies from isolation basin sediments because foraminifera do not live in freshwater conditions.

3. The technique is relatively quick compared to microfossil techniques which rely on time consuming counts and is inexpensive relative to some other geochemical techniques such as biomarker compounds.

4. Diagenesis is thought insignificant for $\delta^{13}C_{org}$, and only small in C/N ratios.

2.6 Oxygen and carbon analysis of foraminifera

2.6.1 Introduction

The isotopes of oxygen and carbon from foraminifera are one of the major proxies used in palaeoceanography reconstructions following the pioneering work of Emiliani (1955) who proposed that shifts in $\delta^{18}O_{foram}$ from calcareous foraminifera were associated with changes in Pleistocene climate and temperature. Changes in ocean benthic foraminifera $\delta^{18}O$ values are believed to represent changes in ice volume (Shackleton and Opdyke, 1973), while fluctuations in $\delta^{13}C$ are related to palaeoproductivity in the oceans (Shackleton, 1977). The use of benthic $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ has not remained restricted to ocean settings. For example, Keith and Parker (1965) discovered that $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ from marginal marine environments were not reliable indicators of palaeotemperature but the isotopic signal was influenced by other factors such as salinity. More recently, Lloyd and Evans (2002), used $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ as a method for reconstructing palaeosalinity changes associated with RSL from a Scottish isolation basin. $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ can be used as palaeosalinity indicators within isolation basins because ocean water and freshwater have markedly different isotopic compositions. It is assumed that the $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ signal in calcareous foraminiferal tests reflects the isotopic composition of ambient water in which they grew. In the following section the links between salinity and $\delta^{18}O_{foram}$ values will be presented followed by a discussion of $\delta^{13}C_{foram}$.

2.6.2 Systematics and background

Oxygen isotopes in water ($\delta^{18}O_w$)

There are three stable isotopes of oxygen: ^{16}O, ^{17}O and ^{18}O with relative abundance of 99.76, 0.04 and 0.20%, respectively. Because of the very low abundance of ^{17}O, oxygen isotope ratios used in palaeoenvironmental reconstruction describe the difference between $^{18}O/^{16}O$. The $\delta^{18}O_w$ value of North Atlantic water is 0 ± 1‰ (SMOW) (Epstein *et al.*, 1953) which is maintained by the circulation of waters through mid-oceanic hydrothermal systems every 30Ma. Deviations away from this value in the surface water are due to the following three processes:

1. Evaporation, which causes surface water to become enriched with ^{18}O because of the preferential removal of the lighter isotope ^{16}O.
2. Formation of sea-ice, which causes new sea-ice to have a higher $\delta^{18}O$ by around 2.57 ± 0.10‰ relative to seawater $\delta^{18}O$ (Macdonald *et al.*, 1995).
3. Addition of meteoric water (water that has previously evaporated from the ocean) to the oceans in the form of rain water, river water and melting

land-ice. The greater the distance meteoric water has travelled from the source region of marine water, the lower the $\delta^{18}O$ value will become due to various processes, therefore precipitation values of $\delta^{18}O$ range across the globe from ~0‰ at the tropics to –62‰ at the poles. However, typically, rainwater originating from precipitation in Northwest Scotland has $\delta^{18}O$ value ranging from –7‰ to –5‰ (Darling *et al.*, 2004). Hence the greater the freshwater influence the lower the $\delta^{18}O_w$ value will become.

Oxygen isotopes in foraminifera

There are 3 main variables that control the isotopic signal preserved in foraminifera during calcite precipitation (Murray, 1991; Rohling and Cooke, 1999) in the marine and brackish environments in which foraminifera live.

1. The isotopic composition of the ambient water mass. This is influenced by processes described above, but especially evaporation and freshwater dilution. Hence the isotopic composition of isolation basin water and the foraminifera living within are directly affected by salinity fluctuations associated with changes in freshwater and marine water inputs to the basin.
2. The temperature of the water during the life of the organism affects the fractionation of ^{18}O and ^{16}O into the test. It is estimated that there is an equilibrium fractionation amounting to –0.2‰ to –0.25‰ per 1°C change, an increase in temperature leading to a light isotopic signature for $\delta^{18}O$ (Epstein *et al.*, 1953). Contemporary, isolation basin seawater temperatures range from 12 to 16°C between spring/summer, (temperature ranges from contemporary data set, see Chapter 7) which leads to an isotopic range of around 1‰ (using the Craig (1965) equation) based on temperature variations alone.
3. Vital effects, such as different growth or calcification rates affect $\delta^{18}O_{foram}$ values and a juvenile chamber can be lower relative to more mature individuals. Changes in carbonate ion concentrations $[CO_3^{2-}]$, such as a decrease in CO_3^{2-} caused by a reduction in pore-water pH may cause a small

enrichment in $\delta^{18}O_{foram}$ (Bemis *et al.,* 1998). To minimise this effect monospecific samples and similar-sized species are used (Rohling and Cooke, 1999)

In summary, the $\delta^{18}O_{foram}$ signal is a reflection of water salinity (ambient isotopic concentration of the water with a range of 0‰ (marine) to –6‰ (freshwater) (values from contemporary data set, see Chapter 7), water temperature in the basin which could cause a range of 12°C to 16°C and species vital effects at the time of carbonate secretion (currently unknown for foraminifera within isolation basins). However, it is likely that salinity will be the dominant environmental variable because of the large variations (salinity range 35 to 0 psu).

Carbon isotopes in water ($\delta^{13}C_{TDIC}$)

The $\delta^{13}C$ signal in basin waters and foraminifera is more complicated and less well understood than $\delta^{18}O$. This is because carbon isotopes are involved in a number of processes, the $\delta^{13}C_{foram}$ signal is related to the TDIC of the water. TDIC is composed of HCO^-_3 (bicarbonate), CO_3^{2-} (carbonate) and dissolved CO_2. At normal seawater pH (7.8-8), HCO^-_3 dominates (Rohling and Cooke, 1999). The $\delta^{13}C$ of marine waters is a balance between the TDIC caused by the primary productivity and remineralization of depleted CO_2 from organic carbon. The average $\delta^{13}C$ of marine TDIC is 0‰ (PDB) (Hoefs, 1997). Global shifts in terrestrial vegetation (C3 or C4) and the large-scale burial and oxidation of organic matter (Rohling and Cooke, 1999) are the two main controlling factors of marine TDIC over long time scales.

Carbon isotopes in foraminifera

On the local scale, changes in $\delta^{13}C_{foram}$ are influenced by four main factors:

1. Changes in surface water productivity. An increase in productivity causes the TDIC to become enriched in ^{13}C, as organisms preferentially take up ^{12}C. When the TDIC becomes depleted in ^{12}C, foraminifera take up more ^{13}C in

the increasingly ^{13}C enriched pool. This causes the $\delta^{13}C_{foram}$ values to increase.

2. Different water masses and circulation patterns. Individual water masses have distinct isotopic signatures. In isolation basins the change in water masses will be caused by the difference between freshwater and seawater. Freshwater is isotopically lighter relative to marine water because it is derived from respiration of isotopically light terrestrial organic matter (as discussed in 2.4.2).

3. Vital effects such as changes in carbonate ion concentration, for example an increase in CO_3^{2-} associated with fluctuations in pore-water pH, will cause $\delta^{13}C_{foram}$ to become isotopically lower (Spero *et al.*, 1997), in a similar way to $\delta^{18}O_{foram}$.

4. Microhabitat effects, for example, the oxidisation of bottom sediment can affect the $\delta^{13}C_{TDIC}$ signal of the pore water. Oxidation causes the release of isotopically light ^{12}C resulting in pore waters becoming enriched in ^{12}C relative to bottom water (Grossman, 1987). Gradients in $\delta^{13}C_{TDIC}$ may reach as much as 1‰ per cm depth within the sediment (Grossman, 1987). Understanding the precise ecological niche of the foraminiferal species being analysed is therefore necessary before interpreting data. Vital effects have a greater impact on $\delta^{13}C$ values than on $\delta^{18}O$ (Murray, 1991).

Previous research

A number of studies have applied $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ as a palaeosalinity proxy to marginal marine environments. One of the earliest investigations was by Corliss *et al.* (1982). *Protelphidium obiculaire* were analysed from a former shallow enclosed sea (Champlain Sea, USA, < 100 m water depth). Samples had lower $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ values with decreasing palaeosalinity, $\delta^{18}O_{foram}$ decreased by around 5‰ and represented a 6psu decrease in salinity caused by meltwater from the deglaciation of the Laurentide Ice Sheet. A similar decreasing trend in $\delta^{18}O$ and $\delta^{13}C$ values from foraminifera and molluscus shells living in the shallow ponds at Lee Stocking Island, Bahamas (Dix *et al.*, 1999) were used to reconstruct trends in RSL over the last 1500 years. Schoning *et al.* (2001) analysed $\delta^{18}O$ from benthic foraminifera across a west-east transect from Skagerrak, central Sweden to the Baltic Sea, to reconstruct changes in salinity associated with the evolution of the region since the Younger Dryas. For example, the $\delta^{18}O_{foram}$ values decrease from +1.5‰ and –1.0‰ from the three western sites, to between –4.5‰ and –9.5‰ from the three site eastern sites around the Yoldia Sea due to the effect of increasing amounts of freshwater reducing the palaeosalinity. Oxygen and carbon isotope ratios from molluscus shells have also been successfully applied to investigations of estuarine environments. In particular Ingram *et al.* (1996) analysed $\delta^{18}O$ and $\delta^{13}C$ from mollusc shells to reconstruct palaeosalinity and palaeoflow trends associated with changes in palaoeclimate of San Francisco Bay since the Mid Holocene. Both $\delta^{18}O$ and $\delta^{13}C$ values of the estuary waters and the molluscs varied systematically as a function of salinity. A similar study was conducted on drowned lagoonal deposits in southern Scandinavia (Bennike *et al.*, 2000). Again, $\delta^{18}O$ values from mollusc shells become lower with decreasing salinity. The mollusc *Mactra isabelleana* has also been shown to have a great potential as a palaeosalinity indicator in the southern hemisphere because $\delta^{18}O$ and $\delta^{13}C$ reflect seasonal changes in the salinity of coastal waters of Buenos Aires, Argentina (Leng and Peace, 1999).

Isotope techniques have been recently applied to fossil Scottish isolation basin sediments using the oxygen and carbon isotopic composition of two foraminiferal species (*Haynesina germanica* and *Elphidium williamsoni*) as a palaeosalinity indicator associated with RSL change from two extended transitional isolation basin sequences (Loch nan Corr and Rumach VI) (Lloyd and Evans, 2002). The species *H. germanica* was found to be the more suitable species for palaeosalinity reconstructions because it mirrored the foraminiferal salinity data from the basin. The trends in the isotopic data matched the biological reconstructions from each site. However, it was speculated that changes in the source of organic matter might be the controlling variable for $\delta^{13}C_{foram}$ and not simply salinity (Lloyd and Evans, 2002).

2.6.3 Rationale

The rationale behind the choice of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ as palaeosalinity indicators was because of the potential to differentiate marine from brackish conditions, as shown by previous studies on a range of marginal marine environments including Scottish isolation basin sediments. However, the $\delta^{13}C_{foram}$ link to salinity is more indirect, $\delta^{13}C_{foram}$ has the potential to identify changes in palaeoproductivity within isolation basin sediments. The study in this thesis will build upon Lloyd and Evans (2002) research; a greater number of environmental variables will be measured (e.g. temperature, pH, dissolved oxygen concentrations of contemporary isolation basin waters) in addition to $\delta^{13}C_{org}$, $\delta^{18}O_{w}$ and $\delta^{13}C_{TDIC}$ to understand the relationship between isotope ratios found within foraminifera and other environmental variables. This study will attempt to understand the controlling variables influencing the $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ signal to salinity, with the objective of providing a more robust interpretation of the $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ record.

2.6.4 Research approach

The application of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ as a salinity proxy will be tested by examining the relationship between the isotopic concentration of basin waters ($\delta^{18}O_{w}$, $\delta^{13}C_{TDIC}$) and the foraminifera species *H.germanica* ($\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$), from the marine-brackish contemporary isolation basins. The contemporary observations will be used to understand the down-core measurement on the species *H.germanica* from fossil isolation basin sediment.

2.7 The application of oxygen isotopes to diatoms

2.7.1 Introduction

The use of siliceous diatom frustules for oxygen isotope analysis ($\delta^{18}O_{diatom}$) was first developed by oceanographers as an alternative proxy for palaeoenvironmental reconstruction when sediments were carbonate poor (Clayton *et al.*, 1972; Labeyrie, 1974; Mikkelsen *et al.*, 1978; Labeyrie and Juillet, 1982; Shemesh *et al.*, 1992). The first applications of the technique were the development of temperature fractionation curves (Clayton *et al.*, 1972; Labeyrie, 1974). More recently, $\delta^{18}O_{diatom}$ has been applied to lacustrine sediments (Leng *et al.*, 2001; Barker *et al.*, 2001). $\delta^{18}O_{diatom}$ has never been applied to marginal marine settings nor has it been used as a palaeosalinity indicator.

2.7.2 $\delta^{18}O_{diatom}$ systematics and background

Diatoms are photosynthetic algae that precipitate a siliceous shell (SiO_2) called a frustule, which is composed of two layers.

1. The outer layer is porous SiO_2 covered by hydroxyl radicals. The oxygen atoms within the hydroxyl radicals are weakly bonded and freely exchange oxygen with waters they are in contact with such as formation waters or laboratory water preparation. The isotopic composition of the outer layer will reflect this mixed signal.
2. The inner layer is composed of biogenic silica secreted as opal ($SiO_2.nH_2O$). This inner layer is denser and less hydrated than the outer layer. Oxygen atoms bond strongly to the silicon atoms and the isotopic composition of this layer is assumed to reflect the condition of silica formation and thus the host water mass ($\delta^{18}O_w$) (Labeyrie and Juillet, 1982).

In lakes at high latitudes diatoms generally bloom in spring and autumn (Reynolds, 1984) but species specific blooms can occur between these periods (Raubischek *et al.*, 1999). The bloom is controlled by nutrient availability, light penetration and convection currents (Kelley, 1997). Due to the microscopic nature of diatoms monospecific ensembles have so far not been analysed. However, $\delta^{18}O_{diatom}$ values from marine or freshwater environments are not believed to be influenced by species specific fractionation effects (Shemesh *et al.*, 1995; Shemesh and Peteet, 1998; Rietti-Shai *et al.*, 1998; Rosqvist *et al.*, 1999). The $\delta^{18}O_{diatom}$ signal is from a bulk sample that reflects the ambient $\delta^{18}O_{w}$ of the main growth periods. Theoretically, $\delta^{18}O_{diatom}$ samples from marine phases of the isolation process will be isotopically higher than samples from the freshwater phase and intermediate values should be recorded from the brackish phases. The controls on marine $\delta^{18}O_{w}$ are discussed in Section 2.6.2. In the freshwater phases the ambient lake water will be influenced by freshwater inputs including, ground water, temperature and evaporation. Little is known about $\delta^{18}O_{diatom}$ fractionation, because the actual number of studies are few and all are based on bulk samples (e.g. Labeyrie and Juillet, 1982; Juillet-Leclerc and Labeyrie, 1987; Shemesh *et al.*, 1995). Estimates of average temperature fractionation range from –0.2 to –0.5‰/°C in ocean waters (Juillet-Leclerc and Labeyrie, 1987; Shemesh *et al.*, 1992) and –0.2‰/°C in freshwater (Brandriss *et al.*, 1998). However, Schmidt et al. (1997) found no regular correlation between temperature and oxygen isotope fractionation from live diatoms in ocean waters, suggesting temperature dependent fractionation is actually established after sediment deposition during diagenesis processes, rather than when the diatom were living. Overall, calibrations for temperature dependence oxygen isotope fractionation between diatoms and water will remain controversial until further work is undertaken.

The main difficulty with this approach technique is extracting pure diatomite fractions from minerogenic rich sediment. Contamination by clay and silt particles can lead to spurious results (Morley *et al.*, 2004). In addition early work was also hampered by poor result reproducibility due to the isotopic exchange of oxygen between silica with hydration water during laboratory preparation (Mopper and Garlick, 1971). Despite these early problems, a number of studies have applied use of siliceous diatom frustules for oxygen isotope analysis as a palaeotemperature proxy in both marine (Julliet-Leclerc and Labeyrie, 1987, Matheney and Knauth, 1989; Shemesh *et al.*, 1992) and lacustrine settings as a tool for reconstructing changes in lake hydrological conditions (Leng *et al.*, 2001; Barker *et al.*, 2001; Rioual *et al.*, 2001) and temperature and isotopic composition of precipitation (Shemesh and Peteet, 1998; Rosquist *et al.*, 1999; Hu and Shemesh, 2003; Jones *et al.*, 2004).

2.7.3 Rationale

The application of $\delta^{18}O_{diatom}$ as a palaeosalinity indicator is a novel application of the proxy. It is thought to be an appropriate method for palaeosalinity reconstruction within isolation basins because $\delta^{18}O_{diatom}$ values will be influenced by similar variables as $\delta^{18}O_{foram}$. Due to the generally high abundance of diatoms in isolation basin sediments, $\delta^{18}O_{diaom}$ will provide an alternative palaeosalinity indicator for sediments that are devoid of calcareous remains. As diatoms are not restricted to marine or brackish environments, unlike calcareous foraminifera, $\delta^{18}O_{diatom}$ will, potentially be able to reconstruct salinity for all stages of an isolation event. In addition, the potential exists to make direct comparisons between $\delta^{18}O_{diatom}$ and $\delta^{13}C_{org}$ and C/N ratios as salinity indicators.

2.7.4 Research approach

Testing the application of $\delta^{18}O_{diatom}$ as a palaeosalinity proxy will be undertaken in a similar manner to $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$, by establishing the relationship between $\delta^{18}O_{diatoms}$ and salinity and temperature, before applying the relationships to down core measurements from fossil isolation basin sediments. Before measurements can be made on any sample, a technique for extraction of pure diatom was developed.

2.8 Strontium isotopes

2.8.1 Introduction

Strontium isotopes ($^{87}Sr/^{86}Sr$) are produced by the *ß*- decay of ^{87}Rb (half life $t_{1/2}$= 4.9 x 10^{10} years) to ^{87}Sr (conversion of a neutron into a proton, with the emission of an electron from the nucleus). The element Sr (atomic number 38) has four naturally occurring isotopes with masses of 84, 86, 87 and 88. They are found in the proportions 0.56%: 9.87%: 7.04%: 82.53% but these vary due to the radiogenic nature of ^{87}Sr (Vierzer, 1989). Radiogenic isotopes differ fundamentally from stable isotopes as they are unaffected by fractionation effects and therefore the potential exists to produce quantitative palaeoenvironmental reconstructions. This is because the atomic weight difference between ^{86}Sr and ^{87}Sr (around 1%) is too small to be fractionated kinetically like the isotopes of oxygen and carbon (differences in atomic weight ^{16}O and ^{18}O; around 11%. ^{12}C and ^{13}C; around 8%). In addition, strontium cannot be metabolized (Reinhardt *et al.,* 1999). This is thought to reduce the potential for biological or kinetic fractionation between isotopes of strontium (Reinhardt *et al.,* 1999)

2.8.2 Strontium isotopic systematics and background

The abundance of the isotope is conventionally expressed relative to the abundance of ^{86}Sr. ^{87}Sr/^{86}Sr isotopic ratios are commonly normalised relative to a standard, such as Atlantic seawater (0.7092), Eimer and Amend $SrCO_3$ (0.70800) and National Bureau of Standards NBS –987 (0.710242), as defined by equation (2). Sr isotope ratios are measured to the sixth decimal place. ^{87}Sr/^{86}Sr ratios can also be expressed in delta notation (δ), as in stable isotope studies (Hess *et al.,* 1986), but despite attempts to standardise the convention notations between stable and radiogenic isotope users, the numeric form is still widely used.

$$\delta^{87}Sr = [(^{87}Sr/^{86}Sr)_{sample}/(^{87}Sr/^{86}Sr)_{standard}\} - 1] \times 10^5 \qquad (2)$$

Traditionally geologists have used Sr for geochronology (Burke *et al.,* 1982; Faure, 1982; Farrell *et al.,* 1995), as an indicator of weathering (Palmer and Edmond, 1989) and a provenance tracer (Yokoo *et al.,* 2004). The use of strontium isotopes (^{87}Sr/^{86}Sr) as a palaeosalinity proxy is a relatively recent adaptation of the technique and is due to the discovery that Sr behaves conservatively during mixing between river and seawater (Palmer and Edmond, 1989; Hodell *et al.,* 1990; Schmitz *et al.,* 1991; Bryant *et al.,* 1995). In order for there to be a salinity signal, $^{87}Sr/^{86}Sr$ ratios in river waters have to be either radiogenically higher or lower than the world wide modern marine value (0.70917) (Schmitz *et al.,* 1991; Ingram and Sloan, 1992).

In order to understand how $^{87}Sr/^{86}Sr$ can be used as a salinity indicator, I will explain how the isotopic composition of seawater and river waters is set. The strontium isotopic composition of seawater is set by the fluctuations in three main sources;

Mid Ocean Ridges (MOR)

Sr in seawater is drawn down towards MOR, where it is precipitated in anhydrite ($CaSO_4$) which is then precipitated at shallow crustal depths. Sr in seawater is replaced by leaching of Sr from the newly formed MOR basalt, which has $^{87}Sr/^{86}Sr$ ratios close to 0.703 (Palmer and Edmond, 1989).

River transport

Rivers transport weathered continental material into the oceans. This process is a net supplier of Sr to the oceans. Sr is dissolved into rivers which pass over igneous and metamorphic rocks. The average $^{87}Sr/^{86}Sr$ from the world's rivers to the oceans is 0.712 $\pm$ 0.001(Palmer and Edmond, 1989) (Palmer and Edmond, 1989). This is the dominant source controlling the flux of Sr to the oceans (Palmer and Edmond, 1989).

Calcium carbonate removal

Strontium is removed from the oceans by the formation of calcium carbonate organisms, which eventually accumulate to form sedimentary rocks. Through the process of pore water dynamics calcium carbonate can recrystallize and return a relatively small portion of this Sr back into the oceans, this returned Sr has a $^{87}Sr/^{86}Sr$ ratio of 0.7087 (Palmer and Elderfield, 1985).

The $^{87}Sr/^{86}Sr$ ratio of the ocean has fluctuated over geological time, caused by changes in global climate affecting weathering and river flows, which has altered the supply of Sr to the oceans. The $^{87}Sr/^{86}Sr$ ratio of the oceans increased monotonically over the last 40 Ma (DePaolo and Ingram, 1985; Hess *et al.*, 1986). Due to the residence time of Sr in the ocean ($\approx 5 \times 10^6$ years) being far longer than it takes for ocean currents to mix the oceans fully (around $\approx 10^3$ year; Broecker and Peng, 1982), $^{87}Sr/^{86}Sr$ has had a constant isotopic composition ($^{87}Sr/^{86}Sr = 0.7091$-0.7092) (Palmer and Elderfield, 1985) and a uniform Sr concentration of 7.9 ppm for the past 400 ka years (Capo and DePaolo, 1990; Palmer and Edmond, 1989; Holland, 1978). The Sr isotope compositions and concentrations of river waters reflect the $^{87}Sr/^{86}Sr$ of the rocks and sediment being eroded in the catchments over which they flow (Wadleigh *et al.*, 1985; Goldstein and Jacobsen, 1987; Palmer and Edmond, 1992). River water can be either isotopically higher or lower than seawater (Schmitz *et al.*, 1991; Ingram and Sloan, 1992). For example, water that has travelled over granite, gneiss, shale and sandstone have higher $^{87}Sr/^{86}Sr$ ratios than water that has travelled over carbonates (Faure, 1986). Limestones also have lower Sr isotopic ratios than marine waters. Volcanic hot springs or evaporites can have similar ratios to modern seawater Sr (Mazzini *et al.*, 1999; Israelson and Buchardt, 1999)

In theory $^{87}Sr/^{86}Sr$ ratios from marine stages of Lateglacial and Holocene isolation basin sediments should record values similar to modern marine $^{87}Sr/^{86}Sr = 0.7091$-0.7092 (Palmer and Elderfield, 1985) while foraminifera from brackish sediment will be more or less radiogenic compared to modern marine values depending on the composition of the freshwater source.

2.8.3 Rationale

The rationale behind the choice of $^{87}Sr/^{86}Sr$ as a salinity proxy for isolation basins sediment is due to the potential of the technique to make quantitative reconstructions between marine and brackish conditions. This is because $^{87}Sr/^{86}Sr$ is not affected by fractionation, temperature or vital effects (Dasch and Campbell, 1970; Schmitz *et al.*, 1991; Reinhardt *et al.*, 1998a) that might have an influence on other proxies such as, $\delta^{13}C_{foram}$, $\delta^{18}O_{foram}$ and $\delta^{18}O_{diatom}$. The ability to make quantitative salinity reconstructions is demonstrated by a number of previous studies from a range of marginal marine environments. For example, Ingram and Sloan (1992) and Ingram and DePaolo (1993) made quantitative estimates changes in the palaeosalinity of San Francisco Bay estuary, associated with changes in the freshwater inflow to the estuary linked to climate change, during the last interglacial and the mid Holocene using $^{87}Sr/^{86}Sr$ ratios from foraminifera and mollusc shells. Reinhardt *et al.* (1998a) successfully used $^{87}Sr/^{86}Sr$ to make quantitative reconstructions of salinity changes on Manzala lagoon, in Egypt's northeastern Nile River Delta, associated with the construction of the Aswan High Dam. Israelson and Buchardt (1999) used the $^{87}Sr/^{86}Sr$ ratio of bivalves to reconstruct trends in palaeosalinity associated with changes in glacial meltwater within Scoresby Sund Fjord, East Greenland over the last interglacial.

2.8.4 Research approach

In order to test $^{87}Sr/^{86}Sr$ as a palaeosalinity indicator from foraminifera, it is necessary to construct a mixing line for $^{87}Sr/^{86}Sr$ from seawater and freshwater from contemporary isolation basin waters and then use the mixing line to reconstruct quantitative palaeosalinity values from foraminifera in a sediment core from the same field area as the contemporary samples.

2.9 Sequential leaching of major, trace and rare-earth elements

2.9.1 Introduction

A debate exists as to whether elemental analysis can be used for salinity reconstructions. For example, changes in boron concentrations were thought to be an indicator of salinity (Levinson and Ludwick, 1966. Boron concentrations are higher in marine water (4.5 ppm) compared to freshwater (0.01 ppm) (Levinson and Ludwick, 1966. Boron is found to decrease linearly in estuaries as a function of increasing dilution of seawater by freshwater (Frederickson and Reynolds, 1959). However, the reliability of boron has been questioned. Fluctuations in boron concentrations are believed to be linked to changes in clay mineral concentrations (Harder, 1970; Perry, 1972). However, multi elemental analysis may potentially overcome some of the problems of using individual elements. A combination of major, trace and rare earth elements (REE) could possibly be used to reconstruct palaeosalinity within isolation basins.

2.9.2 Systematics and background

Major elements

The major (Na, Mg, Ca, Cl, K, Sr, S, and Li) elements are found in higher concentrations in marine water compared to freshwater (Aston, 1978). The basis for major elements as a palaeosalinity proxy is due to the difference between seawater and freshwater. Theoretically, as salinity increases, the elements Na, Mg, Ca, Cl, K, Sr, S, and Li should increase in concentration. For example major elements analysis was applied to trace the influence of terrestrial matter on the bottom and the suspended sediment of Sepetiba Bay, Rio de Janeiro, a shallow coastal lagoon in Brazil (Barcellos *et al.,* 1997). The major elements Ca, Si and K were used to indicate the influence of marine conditions while Ti, Fe and Al were selected as tracers of terrigenous influence.

Trace elements

Trace elements are elements that are found in concentrations of less than 1 ppm. The trace elements As, Ba, Cd, Cu, Co, Mo, Mn, Ni, Pb, U, Zn, V have the potential to be used to reconstruct redox and palaeoproductivity signals in isolation basin sediments. There is evidence to suggest that isolation basins can become anoxic during an isolation event (Snyder *et al.,* 1997; Long *et al.,* 1999). Reconstructing the different redox regimes during an isolation event may further our understanding of isolation basin dynamics. Redox changes could influence how the fauna and flora respond to salinity during these times. The elements: Cd, Cu, Co, Mo, Ni, U, and V have been found to be good indicators of anoxic conditions (Calvert and Pedersen, 1993). These elements enrich in anoxic water because they are scavenged by sulphide and formation of manganese minerals (Sternbeck *et al.*, 2000). Also the trace elements Ba and V have been previously proposed as paleaoproductivity signals in deep sea sediments (Dymond *et al.*, 1992).

A number of studies (e.g. Sternberg *et al.*, 2000; Sohlenius *et al.*, 2001) have used multi elemental analysis to understand the Holocene lithological succession of the sediments from the Baltic Sea from a freshwater to brackish environment and in other sill basins such as the Black Sea and Kau Bay (Middelburgh *et al.*, 1991). Redox sensitive trace elements have been used to characterise the initiation of brackish environments. Both Sternberg *et al.* (2000) and Middelburgh *et al.* (1991) found that certain trace elements (e.g. Mo, Cu and Cd) became enriched in brackish waters because a halocline develops creating anoxic conditions below the halocline.

Rare Earth Elements

REE are the 15 lanthanide elements with atomic numbers ^{57}La through to ^{71}Lu. This group is further subdivided into two groups; low, the first 7 elements with atomic numbers 57-63 La through to Eu, and high, Gd through to Lu. In this study, the two low REE, Cerium (Ce) and Europium (Eu) will be used. Ce and Eu display unique anomalous concentration values (i.e. significantly different positive or negative) in marine compared to freshwater sediments (Armstrong *et al.*, 1999; Owen *et al.*, 1999). This is because Ce and Eu do not form ions that are trivalent (Ce^{4+} and Eu^{2+}) unlike the other lanthanide REE. Their unique behaviour has implications for salinity studies. In theory sediments that were last in contact with marine waters should record either a positive or negative anomalous value, when compared against a series of normalized REE in order of atomic number. This can then be used to reconstruct palaeosalinity trends across an isolation contact. In addition, the nature of the anomaly can be used to further characterise the redox conditions that prevailed during the time of elemental deposition. A positive anomaly can suggest reducing conditions while a negative anomaly indicates an oxidising environment (Elderfield and Greaves, 1982; Wilde *et al.*, 1996; Holser, 1997).

The use of the REE elements Ce and Eu anomalies have mainly been used by geologists looking at whole rock samples to determine the environmental origin of deposits. For example, the use of Ce and Eu help to determine the controversial origin of the Ordovician cherts terrace deposit of Early Palaeozoic age, Southern Uplands, Scotland (Owen *et al.*, 1999). Wilde *et al.* (1996) used the nature of the anomaly (i.e. positive or negative) to determine if redox conditions occurred during eustatic sea-level changes across Ordovician-Silurian boundary deposits from Scotland.

2.9.3 Rationale

The rationale behind using major, trace and REE elements is that marine sediments should record distinctive elemental concentrations and anomalous values (e.g. REE) compared to freshwater sediments. Also certain trace elements will identify possible changes in redox conditions within brackish phases of isolation basin sediments. Multi elemental analysis is an ideal palaeosalinity proxy for Scottish isolation basin sediments for several key reasons:

1. Elemental analysis does not rely on the preservation of biological remains. This technique, therefore, has the potential to reconstruct salinity trends in sites devoid of microfossils or with poor microfossil preservation.
2. Multi elemental analysis will provide more than one line of evidence for salinity and redox changes.
3. The technique is suitable to use on all types of sediment facies. Therefore all stages of the isolation process can be reconstructed, which is not possible when using carbonate proxies from isolation basin sediments.

2.9.4 Research approach

Testing this proxy as a palaeosalinity indicator will be undertaken in a different way compared to the isotopic methods. No contemporary samples will be collected, instead I present a low resolution study and compare the results to a biological salinity reconstruction from the site. This will test if the chemical concentration of the sediment has been retained or identify if remobilisation of elements has overprinted the salinity signal since the sediment was despotised. Contemporary analysis will not be undertaken because absolute concentrations of elements can change from location to location, due to differences in local geology.

2.10 Biogenic silica and total organic carbon

2.10.1 Introduction

To establish if palaeoenvironmental signals in other than palaeosalinity exist within isolation basin sediments a proxy that was ubiquitous to marine, brackish and freshwater environments, needed to be found. Biogenic silica ($BSiO_2$) is a common proxy used in marine and lacustrine environments for palaeoclimate/ palaeoproductivity reconstructions (Colman *et al.*, 1995; Matthewson *et al.*, 1995; Harrris *et al.*, 1996; Xiao *et al.*, 1997; Kaplan *et al.*, 2002). Increasing $BSiO_2$ and Total organic carbon (TOC) have been used in tandem to reconstruct palaeoproductivity and palaeoclimate (e.g. Wagner *et al.*, 2000).

2.10.2 Background and systematics

Biogenic silica

$BSiO_2$ is a measure of amorphous silica (Conley, 1998). Amorphous silica can be produced organically and inorganically: organic silica is produced by diatoms. Examples of inorganic silica formation include hard-pan soil formation (Wilding *et al.*, 1977) and volcanic eruptions (tephra). However, inorganic silica is less common than organic silica especially in aquatic environments (Conley, 1998). Therefore,

$BSiO_2$ is used as a measure of the palaeoproduction of siliceous algae such as diatoms, chrysophyre cysts and sponges. Typically diatoms are the dominant component in most aquatic environments (Conley, 1998). $BSiO_2$ is controlled by the nutrient availability of silica and to a lesser extent by phosphate and nitrate (Harris *et al.,* 1996). $BSiO_2$ is a measure of aquatic productivity of diatoms (Conley, 1988) which has been shown to be directly linked to climate and is assumed to reflect air-temperatures in freshwater lakes. This assumption has been confirmed by contemporary observations from lakes in the central Boreal Forest in Canada (Schindler *et al.,* 1990).

Total organic carbon

Total organic carbon (TOC) is a measure of the total concentration of organic matter in sediments and is believed to be a more accurate measure of organic content than loss on ignition (LOI) (Dean, 1974). LOI can over estimate the amount of carbon especially in sediments with a high clay content because LOI breaks down the lattice clay bonds that form the particle. TOC is a bulk value of the fraction of organic matter that escaped remineralization (Meyer and Teranes, 2001) and therefore is a measure of lake and catchment productivity. Nevertheless, TOC can be diluted by clastic material, for example during catchment erosion (Dean, 1999). TOC provides a secondary measure of basin and catchment productivity which provides an additional line of evidence for the interpretation of the $BSiO_2$ signal.

Previous research

Biogenic silica has previously been applied as a palaeoproducivity indicator in a number of lakes and marine studies. For example, variation in the $BSiO_2$ on large continental lakes such as Lake Biwa, Japan and Lake Baikal, Russia are believed to represent glacial – interglacial cycles (Xiao *et al.,*1997; Colman *et al.,* 1995). Similar phase linking with glacial – interglacial cycles was found in marine cores of North Africa (Matthewson *et al.,* 1995; Harris *et al.,* 1996). On smaller lakes $BSiO_2$ has been shown to reconstruct high-resolution palaeoclimate over the Holocene. For example, Wagner *et al.* (2000) correlated fluctuations in $BSiO_2$ and TOC from two

Holocene lakes in East Greenland to the $\delta^{18}O$ Retland ice core record, indicating that $BSiO_2$ and TOC signals reflected temperature changes during the Holocene including the Holocene climate optimum and Neoglacial cooling. Also $BSiO_2$ was applied to a small freshwater section of an isolation basin in a study in Southern Greenland (Kaplan *et al.*, 2002). The $BSiO_2$ record was believed to be linked to Holocene climate as it corresponded with the GRIP bore hole temperatures (Kaplan *et al.*, 2002). However, the proxy has not been previously applied to marine and freshwater sediments from an isolation basin. It is unknown exactly how the $BSiO_2$ signal in isolation basin sediments will respond to palaeoclimate and changes in salinity. Salinity changes associated with isolation or connection events have been shown to alter the nutrient concentrations within basins and cause blooms of certain diatom species during and after the isolation (Seppä *et al.*, 2000). Therefore changes in nutrient concentration could potentially influence the $BSiO_2$ signal and override any other palaeoenvironmental signal across isolation contact. The interpretation of the $BSiO_2$ record is complicated because of significant changes in salinity due to RSL change. It is likely that the $BSiO_2$ and TOC signal is a combination of the salinity and climate and it depends which environmental factor was dominant through time. By comparing the $BSiO_2$ signal from isolation basins with other palaeoclimate records e.g. ice-cores, the influence of RSL and climate, should be identified.

2.10.3 Rationale

Biogenic silica and TOC have the potential to reconstruct palaeoclimate within isolation basin sediments. The application of $BSiO_2$ and TOC is thought to be a suitable palaeoclimate proxy for isolation basins because the sediments contain abundant diatoms. Further, a number of studies from lacustrine and ocean settings have produced reliable results using $BSiO_2$ and organic carbon concentrations (e.g. Kaplan *et al.*, 2002; Wagner *et al.*, 2000; Matthewson *et al.*, 1995). However, the application to isolation basins sediments may be more difficult due to the problems of minerogenic dilution associated with marine inundation. Therefore the application of $BSiO_2$ and TOC as a palaeoclimatic indicator will be a novel application of the techniques.

2.10.4 Research approach

I will test if trends in the $BSiO_2$ and TOC recorded from fossil Scottish isolation basin sediments represent changes in North Atlantic palaeoclimate. In order to test the proxies ability as palaeoclimatic indicators within isolation basin sediments, the proxies will be applied to two different types of isolation basin sedimentary sequence. For example, a sequence where the isolation process occurred slowly (i.e. over a couple of thousand years) therefore the basin experienced a gradual change in salinity. In contrast to a basin where changes in salinity occurred rapidly across an isolation contact (i.e. within a couple of hundred years). This will test if the high minerogenic inputs due to marine inundation mask the potential of the proxy to reconstruct palaeoclimatic trends. The trends in $BSiO_2$ and TOC records from isolation basin sediments will be compared with GRIP ice-core data and terrestrial palaeoclimate data (e.g. peat and speleleothem) from NW Britain.

2.11 Tephrochronology

2.11.1 Introduction

Conventional and AMS radiocarbon dating has been the method used to underpin the geochronology of Scottish RSL curves from isolation basin sediments (Shennan *et al.,* 2000). However, due to the problems of radiocarbon dating, for example the mineral carbon effect, radiocarbon plateau and potential marine reservoir effect (Lowe *et al.*, 1991; Lowe and Walker 2000; Björck *et al.*, 1996; Wohlfarth, 1996), the chronological controls of RSL reconstruction can only provide an approximate indicator of the actual rate of environmental change. An additional geochronology proxy was sought to verify independently the existing isolation basin geochronology database and assist with the cross-correlations between isolation basins and other palaeoenvironmental archives such as lacustrine, marine and ice-core archives. Tephrochronology was chosen as a suitable technique.

2.11.2 Background and systematics

Tephrochronology is the use of tephra (volcanic ash < 2 mm) for the purpose of dating and correlating archives. Tephra layers produce discrete time-synchronous markers over wide geographical areas. They are able to cross-correlate marine, terrestrial and ice-core archives. As tephrochronology is an age-equivalent dating technique it does not suffer any of the problems associated with radiometric dating proxies. It is neither reliant on organic or feldspar material being present as a medium to date like radiocarbon or luminescence dating. Tephra can be extracted from organic or minerogenic sediment which makes it an ideal proxy for isolation basins (Dugmore and Newton, 1992; Turney *et al.*, 1998, Mackie *et al.*, 2002) and hence will potentially be able to date minerogenic sections of isolation basins which cannot be dated due to the lack of organic carbon or carbonate. A number of Icelandic tephra layers are dated via ice-core years. For example, the Vedde Ash and 11 980 ± 80 GRIP years, and Saksunarvatn ash 10 180 ± 30 GRIP years (Grönvold *et al.*, 1995) providing key marker horizons that are very accurately and precisely dated.

A number of studies have successfully used a variety of Icelandic micro or cryptotephra (ash invisible to the naked eye) layers to precisely correlate Lateglacial lacustrine archives throughout northwest Europe (e.g. Lowe *et al.*, 1999; Mayle *et al.*, 1999; Eriksson *et al.*, 2000). As yet, no published micro-tephra studies have been undertaken upon Scottish isolation basin sediments. The abundance of tephra layers found across the North Atlantic region, which have been extracted from both marine and terrestrial archives, strongly suggests that tephra will exist within Scottish isolation basins. For example, over 17 tephra layers were deposited between 16 000 to 500 cal BP (the age range of isolation basins sediments in Northwest Scotland) and eight have been found in Scottish terrestrial archives (Halfidason *et al.*, 2000; Langdon and Barber, 2001). In addition, a macro tephra deposit of the Vedde Ash tephra layer has been found within the marine section of a Norwegian isolation basin (Bonevick *et al.*, 2001), further suggesting that tephra could be found within Scottish isolation basin sediments. It is likely that only micro tephra horizons will be extracted from Scottish isolation basins because the majority of tephra layers found in Scotland are micro layers which are invisible to the naked eye (Turney *et al.*, 1997). Only one macro layer has ever been found in a Scottish terrestrial Younger Dryas age sediment, on the Isle of Skye (Davies *et al.*, 2001).

2.11.3 Rationale

Identification of tephra layers would provide an independent check on the existing AMS chronologies from each study site. Tephrochronology would provide a means of correlating RSL index points and any other palaeoenvironmental data with other archives across the North Atlantic region such as terrestrial, marine or ice-cores. Hence, tephrochronology would provide a robust chronological framework in which land-ocean interactions from marginal marine environments could be identified, which has important implications for palaeoenvironmental modelling.

Tephrochronology could further help to determine if the AMS dated RSL index points are affected by a marine reservoir effect. The influence of marine reservoir effects on Scottish isolation basin sediments are relatively unknown, though the recent study of Bonevick *et al.* (2001) indicated that no marine reservoir correction is needed in Norwegian isolation basins, the situation may not be different in Scotland. However, the presence of a marine reservoir effect in NW Scotland remains untested. The use of tephra layers would help resolve this issue in Scottish isolation basins. This could be established for Scotland by comparing the radiocarbon date of sediment with the *in situ* tephra layers. Austin *et al.* (1995) used this technique to establish a marine reservoir correction for the North Atlantic during the Younger Dryas chronozone

Certain tephra layers are particularly useful for dating RSL index points. For example, the Vedde Ash layer which falls within the 10 ka BP radiocarbon plateau

(Ammann and Lotter, 1989). A number of isolation basins in Arisaig are isolated around 10 ka BP radiocarbon plateau, for example, Main and Upper basin Loch nan Eala (MLNE and ULNE). The identification of the Vedde Ash horizon may help to date the isolation contacts from ULNE and MLNE more accurately than with existing radiocarbon dating. Also this ash layer has been found in relatively high abundance in lake deposits across North, Northwest and Southern Scotland (Turney *et al.*, 1998; Turney, 1999; Davies *et al.*, 2001) suggesting the Vedde Ash may be deposited in the Arisaig area. In addition, as tephra layers have previously been extracted from Norweign isolation basin sediments (Bondevick *et al.*, 2001), tephrochronology is thought a suitable geochemical proxy to apply to Scottish isolation basins sediments.

2.11.4 Research approach

I aim to extract rhyothlic Vedde Ash shards from freshwater and marine isolation basin sediments. I will try and identify Vedde Ash shards from freshwater sections of isolation basin sediments first. This is because shard preservation and abundance may be adversely affected by tidal scour, causing the abundance of tephra shards to be lower in marine sediment. Once tephra has been identified in freshwater sediment then I will attempt to extract the Vedde Ash shards from marine sediment.

2.12 Summary

Based on previous research of geochemical indicators this chapter has identified a wide range of proxies that might be suitable as palaeosalinity, palaeoclimate and geochronological indicators. As most of these techniques have never been applied directly to isolation basin sediments, a series of pilot studies will be conducted to test their suitability before more detailed studies are undertaken. The next chapter presents the rationale behind the choice of field areas and proxies applied to each field site.

Chapter 3

Site description and selection

3.1 Introduction and sample rationale

Northwest Scotland has been subjected to multiple phases of glacial erosion which have carved the coastline into a series of sea lochs (fjords), rocky headlands and sandy embayments. Consequently, ideal conditions were created for the development of isolation basins. The landscape today has many fossil isolation basins and contemporary isolation basins that vary in size and depth along the north west coast of Scotland (Dickson *et al.*, 1978; Thompson and Wain-Hobson, 1979; Shennan *et al.*, 2000; Laidler, 2002). The field sites for this thesis fall into three areas: Arisaig, Kintail and Knapdale (Figure 3.1). These areas were selected on the basis of the age and altitudinal range of the isolation basins, the preservation and abundance of various groups of microfossil (diatoms and foraminifera), the existence of previous RSL data and the hydrological regime of the contemporary isolation basins. Arisaig was chosen as the main field area; seven fossil isolation basins from Arisaig were investigated (Upper Loch nan Eala, Main Loch nan Eala, Rumach VI, Torr a' Bheithe, Loch Torr a' Bheithe, Loch a' Mhuilinn, Upper Allt Dail An Dubh-Asaid) and one contemporary isolation basin (Rumach Tidal Pond). At Kintail, the fossil isolation basin Loch nan Corr was studied. At Knapdale, only one field site was studied, Craiglin Lagoon, a contemporary isolation basin.

Northwest Scotland was selected as the field area for this thesis because Northwest Scotland contains much of the recent research conducted on isolation basins and some of the longest near-field RSL records in the world (Shennan *et al.,* 1993; 1994; 1995, 1996a,b, 1999, 2000; Lloyd, 2000). Testing alternative geochemical palaeosalinity proxies requires comparison against existing biological salinity reconstructions. Northwest Scotland provides a wealth of field sites where this information exists (e.g. Shennan *et al.,* 1993; 1994; 1995, 1996a,b, 1999, 2000; Lloyd, 2000). Also, in order to understand how the isotope proxies relate to salinity, the contemporary environment needs to be examined. An earlier study by Laidler (2002) identified a number of contemporary isolation basins around Northwest Scotland that were considered suitable analogues for the three main theoretical stages of a basin isolation or connection events illustrated in Figure 1.1 to 1.3. Also, previous research (e.g. Turney, 1999) has shown that micro tephra exists within lake sediments across NW Scotland (e.g. Turney, 1999; Davies *et al.,* 2001). Therefore, there is a high potential for isolation basins from Northwest Scotland to contain micro tephra layers. To test if isolation basins preserve palaeoclimate data, the proxies need to be applied to basins where the salinity changes occurred slowly and field sites where changes in salinity occurred rapidly across each isolation contact. Northwest Scotland provided a number of ideal sites where these conditions have existed.

This chapter presents the rationale behind the selection of the three field areas, the field sites within them and the proxies applied. For each field area the dominant geological and glacial setting and environmental characteristics are discussed.

3.2 Field areas and site descriptions

The location of the different field areas and individual sites are illustrated in Figures 3.1 – 3.2. Individual basins (field sites) are described on the basis of their morphology, sediment, vegetation and tidal regime. Field site characteristics are summarised in Table 3.1 and Table 3.2.

3.2.1 Arisaig

Arisaig is located at the head of Loch nan Ceall and forms the rocky headlands of Keppoch and the Ru Peninsula (Figure 3.1 and 3.2). The geology is dominated by Upper Morar pelites which are cut by a suite of N-S trending Tertiary dolerite dykes, helping to create a landscape of small embayments (Figure 3.3). The area was deglaciated before approximately 16 ka cal yrs (Shennan *et al.*, 2000). This age has been estimated from the oldest dated freshwater organic deposit in the area. During the Younger Dryas chronozone or Greenland interstadial-I (11 – 10 ka BP or (GS-I) the area remained ice free, but the ice limit was only 6 km north of Arisaig (Bennett and Boulton, 1993).

The early deglaciation and absence of Younger Dryas ice, combined with the dyke cut landscape, led to the development of multiple isolation basins across a broad altitudinal range (+0.28 to +36.5 m Ordnance Datum (OD)) and a few contemporary basins, reflecting the pattern of glacio-isostatic uplift. The series of basins form a 'staircase' sequence across the landscape and have accumulated deposits of shallow marine, intertidal, lacustrine and terrestrial sediments since deglaciation of the area (Shennan *et al.*, 2000). The oldest RSL deposits are found at the highest parts of the sequence and the youngest deposits at the base. However, three of the isolation basins (Upper Loch nan Eala, Main Loch nan Eala and Rumach VI) near the base of the sequence are unique in the UK as they preserve a record of RSL history from the Lateglacial through the Holocene (Shennan *et al.*, 1994; Shennan *et al.*, 1996a; Lloyd and Evans, 2002). The multitude of basins with different aged sediments led to Arisaig becoming one of the most well studied areas in the UK for sea-level research (e.g. Shennan *et al.*, 1993, 1994, 1995, 1996a,b, 1999, 2000). The RSL data from Arisaig has contributed to quantitative models of glacial isostatic adjustment, highstands and the timing and rates of global meltwater discharge since the LGM (Peltier, 1998; Shennan, 1999; Shennan *et al.*, 2002).

Arisaig was chosen as the main field area of this study because it contains the highest density of isolation basins (>12) in one compact area with different aged sediments that have detailed biological palaeosalinity RSL reconstructions (Shennan *et al.*, 2000). At all sites the RSL record has been constructed using biological indicators (diatoms, foraminifera, pollen) preserved within the sediment and AMS radiocarbon dated index points. This suite of basins is found in no other area along the coast of NW Scotland. This enabled the new techniques to be applied to the complete temporal range of RSL change reconstructions. This was an important factor in testing $\delta^{13}C_{org}$, C/N ratio and $\delta^{18}O_{diatom}$ analysis as a palaeosalinity proxy (see Chapter 2). The presence of many well-studied fossil basins provided a unique opportunity to compare directly the new geochemical salinity proxies with the biological RSL records. In addition, Arisaig contains a contemporary isolation basin, Rumach Tidal Pond (Figure 3.2). Having a contemporary analogue in the same field area as the majority of my field sites, means that there is an excellent control site to compare fossil data against. It is assumed that the modern analogue experiences similar environmental variables as the fossil basins in Arisaig, for example, local geology, precipitation patterns and vegetation cover. This was particularly important for the $^{86}Sr/^{87}Sr$ proxy where I needed to collect contemporary samples from a basin with identical base geology as the basin sediments to be studied (for further details see Chapter 2).

All of the palaeosalinity (except for $\delta^{13}C_{foram}$ and $\delta^{18}O_{foram}$), palaeoclimatic ($BSiO_2$ and TOC) and the geochronological indicators were tested in Arisaig due to the range of fossil isolation basins preserved within this one area.

3.2.2 Justification of field site selection within Arisaig field area

In order to test $\delta^{13}C_{org}$ and C/N ratios, $\delta^{18}O_{foram}$, $\delta^{13}C_{foram}$, $\delta^{18}O_{diatom}$ and $^{87}Sr/^{86}Sr$ as palaeosalinity proxies, I needed a range of contemporary isolation basins. Also required was a number of fossil basins that contained sediment of marine, freshwater and brackish nature ranging in age from the Lateglacial through to the Holocene.

Arisaig contains a marine analogue: Rumach Tidal Pond. Freshwater and brackish analogues were found in the field areas of Kintail and Knapdale (see sections 3.3 and 3.4). Specifically, a Lateglacial freshwater basin Upper Allt Dail An Dubh-Asaid was used to provide Lateglacial freshwater end-member values. Three basins: Torr a' Bheithie, Loch Torr a' Bheithie and Loch a'Mulliun were selected because they contained Lateglacial marine and freshwater sediment. In addition, the results from Upper Loch Nan Eala, Main Loch Nan Eala and Rumach VI were studied because all three sites contained a mix of freshwater and marine sediment that range in age from Lateglacial through to Holocene. Applying $\delta^{13}C_{org}$ and C/N ratios to these seven field sites, tests the use of these proxies as a palaeosalinity indicators because this will establish if Lateglacial freshwater and marine sediments can be isotopically distinguished from one another, or whether there are other possibly more significant environmental changes other than salinity contained within Lateglacial isolation basin sediments, such as temperature.

To test $\delta^{18}O_{diatom}$ as a palaeosalinity proxy, a field site that was abundant in diatoms throughout the record was required. The pilot study (Chapter 5) established that Upper Loch nan Eala had consistently high diatom abundance throughout the record. In addition, the site was ideal because it contained a range of sediment facies to test the technique upon. Contemporary diatom and water samples were also taken from the three contemporary sites to construct a mixing model and fields of end-member values. The marine analogue in Arisaig (Rumach Tidal Pond) was again used for this proxy. The palaeosalinity proxy $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ was not tested on a fossil site from Arisaig, because there was not a site that contained the foraminiferal species, *Haynesina germanica*, in sufficient abundance for analysis. However, Rumach Tidal Pond was used to collect contemporary foraminifera and water samples to create a marine end-member field for the proxy.

To test $^{87}Sr/^{86}Sr$ as a quantitative palaeosalinity proxy a contemporary Sr mixing model needed to be constructed. Therefore the $^{87}Sr/^{86}Sr$ proxy was tested in Arisaig because it contained a contemporary marine isolation basin (Rumach Tidal Pond) near the main cluster of fossil isolation basins. Rumach Tidal Pond provided marine and freshwater end-member values for a $^{87}Sr/^{86}Sr$ salinity mixing model in Arisaig. The mixing model was used to calibrate the $^{87}Sr/^{86}Sr$ results from the fossil basin. The field sites Rumach Tidal Pond and Ruamch VI, were used to test this proxy. $^{87}Sr/^{86}Sr$ was applied to the Holocene section of the fossil site, Rumach VI, because sufficient foraminifera existed for analysis (Lloyd and Evans, 2002).

Upper Loch nan Eala in Arisaig was also used for the palaeoclimate proxies ($BSiO_2$ and TOC) because the sediment preserved within this basin ranges from the Lateglacial to the Holocene and it experienced rapid changes in salinity across each isolation contact. Therefore this site was ideal for testing the ability of $BSiO_2$ and TOC as a palaeoclimate indicator when there were other significant environmental variables (i.e. salinity) which may have affected the $BSiO_2$ and TOC signal to palaeoclimate.

One of the most widely reported microtephra layers in NW Scotland is the Vedde Ash tephra horizon (11 980 ± 80 GRIP years; Grönvold *et al.,* 1995) which was deposited during the Younger Dryas. The only field area which contained Younger Dryas sediment was Arisaig. The five sites where Younger Dryas sediment existed were chosen for analysis: Torr A' Bhethie, Loch Torr a' Bhethie and Loch a' Mhuillin, Upper Loch nan Eala and Main Loch nan Eala.

The basins analysed from Arisaig will be described in order of decreasing altitude. The sedimentology presented in the description below of each site is from the published core that the original biological RSL reconstruction was made.

3.2.3 Upper Allt Dail An Dubh-Asaid

Upper Allt Dail An Dubh-Asaid (UADD) is the highest basin in the sequence with a sill altitude of + 61.88 m OD. This basin is an infilled freshwater loch, approximately 150 m by 200 m. The basal sediments are dated at 14326-15646 cal BP (Shennan *pers. comm.*). UADD is believed to lie above the limit of the Lateglacial marine limit of this area because no marine diatoms have been found in this basin (Shennan *pers. comm.*). The basin contains a broad mix of freshwater species. The lithostratigraphy of UADD records a simple limnic deposit overlying a sand deposit (Figure 3.4). This basin can no longer be sampled as the Arisaig road bypass has destroyed the site. The basin was used to provide a range of $\delta^{13}C_{org}$ and C/N freshwater Lateglacial end-member values. Geochemical analysis was conducted upon the core that had been used for diatom analysis and therefore no cross-core correlation was required.

3.2.4 Torr a' Bheithe

Torr a' Bheithe (TB), is a fossil basin with a sill at +33.2 m OD, it is approximately 200 m long by 100 m wide (Figure 3.5). TB records the Lateglacial RSL fall in this area. Based on the diatom flora, TB became isolated from the sea at 15329 – 14595 (15033) cal yr BP (Shennan *et al.,* 2000) (bracketed date = mean date) (Figure 3.6). TB has a relatively simple lithostratigraphy. There are four main zones and, based on the diatom flora, the basal minerogenic zone is marine in origin. This is overlain by a freshwater limnic deposit at 777 cm. However, the limnic deposit contains a small clastic zone (Zone 3) from 745 to 740 cm. This zone could possibly relate to Younger Dryas sediment, due to the lack of marine or brackish water diatom species in a minerogenic zone of Lateglacial age (Shennan *et al.,* 2000) (Figure 3.5). Zone 4 is a freshwater limnic deposit. A 50 mm diameter Russian core was taken, parallel to the one previously examined (Shennan *et al.,* 2000). Figure 3.6

provides a detailed lithostratigraphic description of the new Russian core. Tephra, $\delta^{13}C_{org}$ and C/N analyses were carried out at this site.

3.2.5 Loch Torr a' Bheithe

Loch Torr a' Bheithe (LTB) is a partially infilled fossil basin approximately 200 m long and 100 m wide. LTB is located directly below Torr a' Bheithe the; altitude of the sill is +24.0 m OD (Figure 3.7). Based on the diatom and foraminiferal analysis, LTB became isolated from the sea at 15251 – 14435 (14843) cal yr BP (Shennan *et al.,* 2000) (Figure 3.8). LTB has a similar lithostratigraphy to TB, with two main zones. Based on the diatom flora and foraminiferal assemblages, the lower clastic zone records marine conditions; this is overlain by a freshwater limnic deposit at 577 cm (Shennan *et al.,* 2000). A new 50 mm diameter Russian core was taken parallel to the old core. Figure 3.7 provides a detailed lithostratigraphic description of the new core. The limnic sequence from the new core contains a 2 cm, sand lens. As with TB, this deposit is assumed to be Younger Dryas in origin. Tephra, $\delta^{13}C_{org}$ and C/N analyses were undertaken from this basin.

3.2.6 Loch a' Mhuilinn

Loch a' Mhuilinn (LAM) is a partially infilled fossil basin approximately 350 m long by 200 m wide (Figure 3.9). The altitude of the sill is +15.5 m OD. Based on the diatom flora LAM was isolated between 14882 – 14153 (14490) cal yrs BP (Shennan *et al.,* 2000) (Figure 3.10). LAM has two main lithostratigraphic zones. Based on the diatom flora, the minerogenic zone from the base of the core records marine conditions. The overlying zone is a limnic deposit at 647 cm (Shennan *et al.,* 2000). However, unlike Loch Torr a' Bheithe or Torr a' Bheithe (see below), no clear Younger Dryas lithostratigraphic zone can be identified. A 50 mm Russian core was taken parallel to the old core near the loch edge. Figure 3.10 provides a detailed lithostratigraphic description of the new core and correlation summary. Tephra, $\delta^{13}C_{org}$ and C/N analyses was carried out at this basin.

3.2.7 Upper Loch Nan Eala

Upper Loch nan Eala (ULNE) is a fossil isolation basin approximately 500 m long by 175 m wide. The altitude of the rock sill of ULNE is + 6.27 m OD (Figure 3.11). The diatom flora has been previously examined to produce a RSL reconstruction for this site (Shennan *et al.*, 1994) (Figure 3.12). Seven zones can be identified, based on the diatom flora and lithostratigraphy. This site experienced a fall in RSL at 12645 –12117 (12420) cal yr BP to a subsequent minimum, some time after the low point recorded by the transition from marine (Zone 1) to freshwater conditions (Zone 2). A following rise in RSL led to the inundation of the basin by marine water at 9433– 9051(9312) cal yr BP by the transition from Zone 2 to the clastic Zone 3. Conditions during the formation of Zone 3, range from brackish to brackish marine. At 7543 – 7388 (7495) ka cal BP a freshwater diatom flora indicates a short lived RSL fall (Zone 5), leading to the isolation of the basin. This event is not interpreted as a regional sea-level change but a local change to ULNE marine conditions rapidly returned until 4868 – 4579 (4832) cal yr BP when the final isolation of the basin occurred due to RSL fall (Zone 6) (Shennan *et al.*, 1994). The basin subsequently infilled (Zone 7). For this study a new 6 m piston core was extracted near LNE 66/67 coring site (Shennan *et al.*, 1995). Figure 3.12 provides a detailed lithostratigraphy of the new core. $\delta^{13}C_{org}$ and C/N ratio, $\delta^{18}O_{diatom}$, biogenic silica and tephra analyses were undertaken at the site.

3.2.8 Main basin Loch nan Eala

Main basin Loch nan Eala (MLNE) is located seaward of ULNE, lower in the staircase sequence, with a sill altitude at + 3.20 m OD (Figure 3.2 and 3.13). The basin is approximately 800 m long by 200 m wide and has a small freshwater loch towards its northern end, which is surrounded by freshwater marsh deposits. The loch has been reduced in size by the construction of a canal in the mid-19th century. The diatom flora has been used previously to produce RSL reconstructions for this site (Shennan *et al.*, 1994) (Figure 3.14). Based on the diatom flora, the basal clastic zone records marine conditions.

The transition to the limnic deposit represents a sea-level regression, dated 12347 – 11347 (12060) cal yr BP. A subsequent transgression is dated at 10013 – 9689 (9925) cal yr BP by the transition from Zone 3 to the clastic Zone 2. The final isolation of the basin, recording the late Holocene fall in sea-level, is dated at 3831 – 3566 (3689) cal yr BP, at the transition between Zone 2 and the limnic Zone 1. A new 50 mm diameter Russian core was taken near the original coring site (Shennan *et al.,* 1995). Figure 3.14 provides a detailed lithostratigraphy of the new core. $\delta^{13}C_{org}$, C/N ratio and tephra analyses were undertaken at this site.

3.2.9 Rumach VI

This is the lowest fossil basin in the Arisaig sequence with a sill altitude of + 3.80 m O.D. and provides a constraint on the RSL minimum in the early Holocene (Shennan *et al.*, 1999, 2000). Rumach VI is approximately 4 km east of MLNE (Figure 3.2 and 3.15). The basin is approximately 500 m long and 200 m wide. Diatoms, foraminifera and dinoflagellate cysts have been used previously to produce RSL reconstructions for this site (Shennan *et al.,* 1999a; Lloyd and Evans, 2002) (Figure 3.16a,b). Based on the diatom flora the basal clastic zone records marine conditions. The transition to the limnic deposit represents a sea-level regression dated 12378 – 11748 (12140) cal BP. A subsequent transgression is dated at 9962 - 9532 (9750) cal BP by the transition from Zone 3 to the clastic Zone 2. Based upon the foraminiferal fauna (Lloyd and Evans, 2002) Zone 2 records a transition from marine to increasingly brackish environment. The final isolation of the basin records the late Holocene fall in sea-level at 2856 – 2739 (2763) cal yr BP.

Despite the detailed biological data from this site, the sedimentary record is complex due to the morphology of the basin (Figure 3.17). The basin can be divided into two sections because of a suspected dyke (lower than the sill of the basin) that passes north to south through the basin. The sediment deposited directly behind the sill only preserves data from Zones 1 and 2. The sediment deposited behind the dyke towards the eastern end of the basin preserves sediment from all four zones. The deepest sediments of the site are found in this section, they are over 11 m thick. Sediment will be analysed from the eastern end of the basin because it preserved the full RSL record for the site. Two cores were used for analysis: one core records the Lateglacial RSL fall and rise and a second core records the Holocene RSL fall. The two cores overlapped each other across Zone 3 when combined together. An added advantage of using the Holocene core was that Lloyd and Evans (2002) had analysed this core. Therefore, problems of cross-correlation with the foraminiferal data were eliminated and direct comparison between the different types of isotopic data could be made. Only the Lateglacial core had to be cross-correlated with the original diatom summary diagram from this site (Shennan *et al.*, 1999), Figures 3.16a and 3.16b are a summary of the lithostratigraphy of both cores and the measurements taken down core.

3.2.10 Rumach tidal pond

Rumach Tidal Pond (RTP) is the final step in the Arisaig isolation staircase. The basin is located at the head of the Ru Peninsula approximately 0.25 km east of Rumach VI (Figure 3.1 and 3.2). RTP is a fully marine contemporary isolation basin which is connected to the sea loch, Loch nan Ceall, through two sills. RTP is approximately 300 m wide and 50 m long (Figure 3.18 and Figure 3.19). The altitude of the lowest sill is +0.27 m OD, this is close to current mean tide level (MTL) +0.3 m OD (Zong, 1997). Fresh water enters the back of the basin though two streams, which drain the surrounding grazed catchment. The basin vegetation is dominated by a few seaweed species; *Bladderwrack*, *Cladaphora rupestris* and *Monostroma grevillei,* which are common around the coastline of NW Scotland. The dominant sediment in the centre of RTP is shingle and coarse sand, however, a silty patch has developed in the north/north eastern end of the basin. The basin receives a marine influx during every high tide event in the tidal cycle including neap tide (MHWNT = + 1.18 M OD). The mean spring tidal range is 3.3 m in this area. The mean high water spring tide

(MHWST) is +2.4 m OD, the altitude of highest astronomical tide (HAT) is +2.9 m OD (Zong, 1997). Figures 3.20 are summaries of the hygrological profiles from the basin. The salinity of the basin is fully mixed at high tides around 32/33 psu (practical salinity units) this is consistent with the salinity of Loch nan Ceall which is approximately 32 - 33 psu. During low tides, salinity can become reduced to 30 psu near the freshwater inputs. RTP represents Stage 2 in Figure 1.1. Despite the site being ideally located in relation to other Arisaig isolation basins, a disadvantage of RTP is the relatively small size and shallow water depth compared to the fossil basins. For example, Rumach VI and UNLE would have had water depths of +10 m (height of sill minus known marine limit at a specific point in time such as the Lateglacial). However, this is a common problem with contemporary isolation basins across NW Scotland (Laidler, 2002). Water samples were collected for $\delta^{18}O_{w}$, $\delta^{13}C_{TDIC}$, $^{87}Sr/^{86}Sr$ analysis and surface sediment samples for $\delta^{13}C_{org}$, C/N ratios, foraminifera and diatoms.

3.3 Kintail

Kintail was chosen as a location for this study because it contains a site (Loch nan Corr, LNC) (Figure 3.1, 3.21) with an extended Holocene isolation sequence and a freshwater loch that could be used as a freshwater analogue. Kintail lies within the Younger Dryas ice limits (Bennett and Boulton, 1993) and so sediment from this area will only record Holocene RSL change. Over 7 m of sediment accumulated during 6000 years and records the gradual change of LNC from a fully marine to a fully freshwater environment. Due to the site's high sedimentation rate (1 mm/yr), a high-resolution archive of Holocene RSL change is preserved. Hence, LNC is a unique archive that provides a rare opportunity to examine in detail the isolation processes of a basin during a RSL fall. This is unusual because typically isolation or connection events occur rapidly and are only recorded within one or two centimetres of sediment. Moreover, LNC also has abundant foraminifera preserved within the sediment making the site an ideal location for $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ analysis. In addition, LNC provided the opportunity to test the reproducibility of $\delta^{13}C_{org}$ and C/N ratios in a field area other than Arisaig, an essential test for any new proxy. Therefore, a range of palaeosalinity proxies and palaeoenvironmental (e.g. $\delta^{13}C_{org}$, C/N, $\delta^{18}O_{foram}$, $\delta^{13}C_{foram}$, $BSiO_2$ and TOC) could be compared at this one site. Biogenic silica analysis was also carried out upon LNC because of the potential to reconstruct a high-resolution archive of Holocene palaeoenvironmental change from a site where the salinity change was slow.

3.3.1 Loch nan Corr

Loch nan Corr, Kintail (LNC) (NG 9422 2107), is a partially infilled fossil basin approximately 500m by 200 m with a rock sill at +2.70 m OD (Figure 3.22). LNC can be divided into two field sites, an infilled fossil basin and a contemporary freshwater analogue. The contemporary freshwater loch will be described first then infilled basin.

A shallow freshwater loch is located at the northern end of the site. The loch is approximately 200 m long, 100 m wide and has a maximum depth of *c.*60 cm. The nearest available tidal predictions from Dornie Bridge suggest this basin should be brackish as the HAT is +0.54 m above the sill, although MHWST = + 2.62 m OD. However, multiprobe measurements in May and October 2002 record a salinity of 0 psu which categorise this basin as a fresh loch, this is supported by the aquatic flora. The mismatch must have been caused by either an inaccurate levelling of the sill height or by a difference in the local tidal regimes between LNC and Dornie Bridge (10 km away). The loch has one major freshwater input, which drains into the back of the basin, and has an outlet over the rock sill. The vegetation around the loch varies from freshwater marsh to mixed woodland. The edge of the basin is dominated by the aquatic macrophytes *Hymphea alba* and *Equisetum fluviatile*. The loch represents Stage 4 of the isolation process illustrated in Figures 1.1-1.2. This loch was used as the freshwater analogue, as it provided freshwater end-member values for $\delta^{13}C_{org}$ C/N ratios and $\delta^{18}O_w$ and $\delta^{13}C_{TDIC}$.

Foraminifera, thecamoebians and $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ have been used previously to produce a RSL reconstruction from the fossil isolation basin at this site (Lloyd, 2000; Lloyd and Evans, 2002) (Figure 3.23). Marine inundation occurred at this site between 9599 - 9278 (9512) cal yr BP, the marine regression started from around 8129 – 7947 (8036) cal BP but it did not become finally isolated until between 733 - 554 (663) cal BP (Lloyd, 2000). Based on the foraminiferal fauna, the basal sandy zone records brackish conditions. An organic/silt limus zone developed at 9132- 9531 cal yr BP and represents an increase in marine inundation to the site. Three more zones overlie Zones 4, each one increasing in organic content up core. Between 6733 – 7208 (6920) to 4151-4780 (4415) cal yr BP a stable brackish environment prevailed. From 4151-4780 cal yr BP the basin experienced a gradual reduction in salinity. The final zone presents the eventual marine withdrawl from the basin at 554-773 (663) cal yr BP. This was marked by the development of an organic rich limus with visible plant remains. A new piston core was taken parallel to the original core (Lloyd, 2000) described above. Figure 3.23 illustrates the lithology of the new core and the measurements taken.

3.4 Knapdale, Argyll

Knapdale was selected as a field area because it contains one of the few known contemporary brackish isolation basins, Craiglin Lagoon, of comparable size (but unfortunately not depth) to fossil isolation basins (Figure 3.1, 3.24). Craiglin Lagoon was believed to contain foraminifera (Laidler, 2002), which were needed to characterise brackish values for $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ analysis. Craiglin lagoon provided contemporary data on the understudied brackish phase for the salinity proxies: $\delta^{13}C_{org}$, C/N ratios, $\delta^{18}O_{foram}$, $\delta^{13}C_{foram}$ and $\delta^{18}O_{diatom}$.

3.4.1 Craiglin Lagoon

Craiglin Lagoon (NR 775 878) is a brackish water basin situated at the head of the sea loch, Loch Sween, 30 miles south of Oban. The basin is 500 m long, 300 m wide and 1.2 m deep at it deepest point. The sill is an artificially straightened culvert, with an altitude +1.42 m OD (Laidler, 2002). The vegetation surrounding the basin is dominated by the aquatic macrophyte, *Equisetum fluviatile*. Multiple ephemeral streams drain the surrounding pine forested catchment, however, a small freshwater spring was observed in the channel to the east of the culvert (Figure 3.25).

Marine inundation only takes place at high water during mid cycle and spring tides (MTL at Carsaig Bay, the nearest tide gauge to this site, is 0.47 m OD; MHWST of + 1.29 m OD and HAT of + 1.64 m OD) (U.K.H.O., 2002). The salinity of this basin varied between 14 to 32 psu in time and space (Figure 3.26).

Multiprobe measurements of Craiglin showed that this basin was ventilated by marine water during high water of the spring and mid-cycle high tides. No inundation was observed during neap tides. The multiprobe investigation showed that the basin was stratified. Figures 3.26 are summaries of the hygrological profiles from the basin. During August 2002, the salinity outside the sill was 33 psu while in the centre of the basin the surface water was ~15 psu, grading to ~29.5 psu between 60-100 cm depth. In October 2002, (7/10/02 Spring tide – High tide) a similar situation was observed but the degree of stratification was less pronounced. Surface water salinity had increased to ~25psu, below 60 cm the salinity had remained ~29.5 psu. The decrease in stratification could be attributed to an increased wind stress between summer and autumn causing greater surface mixing. The stratified water column has possible adverse implications for the accumulation of sea-level indicators; samples may be non contemporaneous and be affected by anoxic processes. The measurements clearly indicate the basin contains brackish water and so

Craiglin Lagoon provides a good contemporary example of the latter stages of isolation, equivalent to Stage 3 of the isolation process illustrated in Figures 1.1-1.2. Observations from this basin will lead to a better understanding of a poorly understood phase of the isolation process.

3.5 Summary

The three field areas were chosen because they contained a range of fossil and contemporary isolation basin environments that were necessary to test the aims of this thesis. Table 3.3 is a summary of combination of chemical and isotopic proxies tested at each field site. In total seven, fossil basins were used to test $\delta^{13}C_{org}$ and C/N as a palaeosalinity proxy. These were the easiest proxies to apply to isolation basins sediments because they are not reliant on the preservation of particular microfossil remains. Consequently, comparisons could be drawn with at least one or more palaeosalinity proxies at a variety of field sites. For example at LNC, $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ could be compared with $\delta^{13}C_{org}$ and C/N. While at Rumach VI, $\delta^{13}C_{org}$ and C/N could be compared with $^{87}Sr/^{86}Sr$ and with $\delta^{18}O_{diatom}$ at ULNE. $^{87}Sr/^{86}Sr$ analysis will be carried out in Arisaig because a contemporary isolation basin was nearby to calibrate the proxy. $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ analyses were undertaken at LNC because of the high abundance of monospecific foraminiferal species. $\delta^{18}O_{diatom}$ was carried out on the field site ULNE because of the site's relatively high abundance of diatom flora available for extraction throughout the RSL record from this basin (see Chapter 5 pilot study). Biogenic silica analysis will be undertaken at ULNE and LNC because of the age of the sediment at each field site. Potentially, a palaeoenvironmental record extending from the Lateglacial through to the late Holocene could be contained within ULNE. By analysing LNC a high-resolution archive of Holocene palaeoenvironmental change could be created. Tephrochronology was only applied to Arisaig basins because it was the only field area with sediment of Younger Dryas age. This was necessary if the

Vedde Ash (11 980 ± 80 GRIP years Grönvold *et al.*, 1995) marker horizon was to be identified.

Chapter 4

Methodology

4.1 Introduction

This chapter presents the detailed methodologies employed for all the proxies used in this thesis. In addition it explains how and when the different aspects of the field data (e.g. coring, contemporary plant, sediment and water samples) were collected.

4.2 Fieldwork

Fieldwork was undertaken during five separate trips to Northwest Scotland between February 2000 and October 2002.

The fieldwork undertaken comprised two main parts:

1. A program of core collection from field sites in Arisaig and Kintail.
2. Observations from the contemporary isolation basins including, detailed studies of their hydrological parameters and collection of organic matter from within and around the contemporary basins.

Core collection

A number of field sites were re-cored because insufficient material remained for analysis from pervious investigations. New 1 m length piston cores were taken from Upper Loch nan Eala and Loch nan Corr. A 50 mm diameter Russian corer was used to collect material from Torr a' Bhethe, Loch Torr a' Bheithe, Loch a' Mhuilinn and Main Loch nan Eala (Figure 3.2 and 3.20). All new cores were taken near the site of cores previously analysed for microfossils (Shennan *et al.*, 1994; Shennan *et al.*, 2000; Lloyd, 2000). After extraction cores were described using the Troels-Smith (1955) lithostratigraphic system. Cores were collected in February and September 2001.

Contemporary isolation basins

In order to understand the geochemical signal from isolation basin sediments, I needed to examine a range of contemporary isolation basins with different hydrological regimes. The three isolation basins studied each represented a key end member stage in the isolation process. Rumach Tidal Pond (RTP) is a fully marine basin (Stage 4 Figure 1.1 Chapter 1), Craiglin Lagoon is a brackish basin (Stage 3 Figure 1.1) and Loch Nan Corr (LNC) is a freshwater loch (Stage 1 Figure 1.1) (see Chapter 3, for further details). In order to calibrate and determine the relationship of the each geochemical proxy to salinity, detailed hydrological data were collected (salinity, temperature, oxygen content, pH), sedimentary and water samples. Hydrological measurements were made during May, August and October to determine the influence of seasonal effects on the isotopic water geochemistry. A transect of sample stations were made across each basin (Figures 3.17, 3.20 and 3. 23).

Hydrological profiles

Hydrological profiles were taken using the Ocean Seven 301 Multi Parameter Senator in May and August 2002. Due to technical problems another instrument had to be used, the YSI-MPS 556 probe (in October 2002). The YSI-MPS 556 probe recorded the same parameters as the other CTD probe except for depth. Depth was calculated by marking the cable attached to the probe with fluorescent tape every 20 cm from the head of the sensors. Both probes automatically calculated salinity from the conductivity measurements (Lewis, 1978). The accuracy of salinity, temperature and pH was 1‰, 0.01°C and 0.05 pH (1SD), respectively for both using the Ocean Seven 301 Multi Parameter Senator and also the YSI –MPS 556 probe.

4.3 Organic carbon isotopes and C/N ratios

Collection of contemporary organic material

All the current major aquatic macrophytes and terrestrial macrophytes were collected from within and around the edge of the contemporary isolation basins. Samples were washed in deionised water to remove soil/sediment and then air dried. The samples were freeze-dried using liquid nitrogen and homogenized in an agate pestle and motor. Bulk surface sediment was collected from the contemporary basins using a box grab sampler. The upper 2 cm of the sediment was collected in labelled self-seal plastic bags, and oven dried prior to homogenisation in agate.

Subsampling of cores

Cores were subsampled at a minimum of 8 cm intervals for % Total Organic Carbon (TOC) and total organic nitrogen measurements, from which C/N ratios were derived and $\delta^{13}C_{org}$. At all transitional boundaries the sampling resolution was increased to 1 or 2 cm intervals.

Preparation of organic material for $\delta^{13}C_{org}$ analysis

The procedure followed was the standard method adopted by the NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth. A sample of 2 cm^3 of sediment was placed in a 50 ml vial. In order to remove carbonate from the sample, 50 ml of 5% HCL (Analar grade made up with deionised water) was added for a minimum of 12 hours. Samples were washed by filtering three times with 50 ml of deionised water through a Whatmans No. 41 filter paper. Filter apparatus was washed with decon solution (again made up with deionised water), and rinsed with deionised water before and after use. The samples were oven dried at 60°C, and homogenised in an agate pestle and mortar. For the $\delta^{13}C$ and C/N measurements, around 1 mg of carbon was used. The amount of sample depended on the percentage of organic material which was measured by loss-on-ignition data (Ball, 1964). Each sample was then weighed using a Santorious microbalance into tin capsules which were sealed and placed in a desiccator prior to analysis.

$\delta^{13}C_{org}$ and C/N measurements

Percentage Carbon and Nitrogen was measured using a Carlo Erba elemental analyser. The Carlo Erba is calibrated using an internal acedanalide standard. Replicate analysis of samples gave a precision of $\pm$ <0.1 ‰ (1 SD). $^{13}C/^{12}C$ analyses were performed by combustion using a Carlo Erba 1500 on-line to a VG Triple Trap and Optima dual-inlet mass spectrometer. $\delta^{13}C$ values were calculated to the VPDB scale using a within-run laboratory standard (cellulose, Sigma Chemical prod. no. C-6413) calibrated against NBS-19 and NBS-22.

4.4 Oxygen and carbon analysis from foraminifera

As with the $\delta^{13}C_{org}$ and C/N ratios contemporary samples were required to calibrate the relationship of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ of *H.germanica* to salinity. Surface sediment and water ($\delta^{13}C_{TDIC}$ and $\delta^{18}O_{w}$) samples were collected from the contemporary isolation basins. The fossil isolation basin sediments from Loch Nan Corr (LNC) were sampled at 8 cm intervals for *H.germanica*.

Collection of contemporary water samples for $\delta^{18}O_{w}$, $\delta^{13}CTDIC$

Bottom and surface water samples were collected in clean 100 ml leak-proof Nalogene bottles from inside and directly outside the sill, and from any stream entering the basin of RTP and Craiglin Lagoon. Samples were taken at high and low tides. Sample stations are illustrated in Figure 3.17, 3.20 and 3.23). Total dissolved inorganic carbon (TDIC) for $^{13}C/^{12}C$ analysis was precipitated on site by the addition of $BaCl_2$ + NaOH. Untreated samples were also collected for $^{18}O/^{16}O$. As soon as possible after collection of the C sample, 15 ml of $BaCl_2$ solution was added. The bottle was shaken and then the top sealed with electricians tape. Samples were stored in a refrigerator at 4°C prior to laboratory analysis.

Analysis of $\delta^{18}O_w$ and $\delta^{13}C_{TDIC}$ samples

Carbon samples were filtered through fibreglass filter papers and washed three times with deniosed water. Samples were then dried and homogenised in an agate pestle and mortar. Analysis of TDIC $\delta^{13}C$ followed the standard equilibration method- samples were reacted with anhydrous phosphoric acid in a vacuum by leaving overnight at 25°C. Samples were then degassed, librating CO_2. Liquid nitrogen was used to contain the CO_2 and separate it from water vapour. Oxygen samples were analysed using the equilibration method for oxygen (Epstein and Mayeda, 1953). Values are reported as per mil (‰) deviations of the isotope ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) from standard VSMOW for oxygen and VPDB for carbon water samples. Analytical precision is <+/- 0.1 ‰ for TDIC for $\delta^{13}C$ and <+/- 0.1 ‰ for $\delta^{18}O$. The water samples were analysed using a VG SIRA mass spectrometer.

Foraminifera

Approximately 12-20 individuals of species *H.germanica* were picked in deionised water. Between 60–70 µg of sample were weighed into glass buckets. The isotopic analysis was carried out using an OPTIMA mass spectrometer with an ISOCARB facility. The analytical reproducibility of standards is better than 0.1‰ (1 SD) for both $\delta^{18}O$ and $\delta^{13}C$. Values are reported as per mil (‰) deviations from the international standard for carbonates VPDB (Vienna-Pee Dee Belemnite) scale. Samples were analysed on the VG SIRA mass spectrometer.

4.5 Oxygen isotopes ratios on diatoms

Collection of contemporary samples

Contemporary diatom samples were collected from surface sediment samples from the three contemporary isolation basins (Figure 3.1). Data from the hydrologic profiles and $\delta^{18}O_w$ water samples described above were used to establish the relationship of $\delta^{18}O_{diatom}$ to salinity.

Preparation of diatom samples

The procedure for sample preparation was devised as part of the research into $\delta^{18}O_{diatoms}$. The method is an adaptation of Turney (1998) specific gravity tephra extraction method.

1. Place 2 cm^3 of sample in a clean 50 ml plastic vial and add 30 ml of 30% Hydrogen Peroxide (H_2O_2 analar grade made up with deionised water) to each sample. Place in a water bath (~200°C) until the liquid has tuned transparent. Wash H_2O_2 off by centrifuging the samples twice with deniosed water at 4500 rpm for 4 minutes. The centrifuge brake rate was set at 0.
2. Sieve the sample with deionised water though a 63 µm and 15 µm mesh. The > 15 µm fraction is decanted in to a 6 ml centrifuge tube. Additional water is removed by centrifuging the sample at 4500 rpm for 4 minutes.
3. 6 ml of sodium polytuntage with a specific gravity of 2.2 gcm^{-3} is added to the sample and shaken well. The sample is then centrifuged at 2500 rpm for 20 minutes. The brake rate of the centrifuge was set to 0. This allowed the solution to spin down slowly and preserve the 'float' (< 2.2 gcm^{-3} fraction).
4. Taking care not to disturb the 'float' the sample was then decanted in to a new 6 ml centrifuge tube.
5. Steps 3 and 4 are then repeated once more.
6. The sodium polytungstate must be removed from all sediment or it will affect the purity of the samples. All sediments that had been in contact with sodium polystungstate were washed a minimum of three times with 10 ml of deionised water. Samples were centrifuged for 4 minutes at 4500 rpm. The brake rate of the centrifuge was set at 4.

7. The floated samples were dried at 60°C.
8. The purity of the sample was checked by optical microscopy.

Analytical procedures

A minimum of 5 mg of purified diatoms was weighted into a capsule. Where individual samples did not contain sufficient material, neighbouring samples were bulked together. Samples underwent a prefluorination step using the reagent chlorine trifluoride (ClF_3) at 250°C for 6 minutes before the full reaction at 450°C for 14 hours with an excess of ClF_4. This method ensures that both the minor clay and hydrous portion of the diatomite was removed during prefluorination. A plateau is then reached beyond which $\delta^{18}O$ value is stable. The oxygen liberated was then converted to CO_2 (Clayton and Mayeda, 1963). Samples were analysed where possible up to 3 times. A standard laboratory quartz and a diatomite control sample (BFC_{mod}) were used for calibration. BFC_{mod} had a mean variance of ± 0.5% for the first batch of samples and ±0.7% for the second batch of samples during the period of analysis. All values are quoted to 1 SD. $^{18}O/^{16}O$ ratios were measured on a OPTIMA mass spectrometer. Values were normalised to laboratory standards and NBS28, and corrected according to Craig (1957) and Deines (1970). The data are presented as per mil (‰) deviations from V-SMOW.

4.6 Strontium isotope ratios

Contemporary sampling

Water samples from the basin and the freshwater and marine inputs into RTP were collected in water tight Nalogene bottles. Surface samples were taken for foraminiferal samples. The salinity of the basin and the freshwater inlets of RTP were recorded with an Ocean Seven 301 Multi Parameter Senator in August 2002.

Preparation of water samples

Approximately 30ml of each sample were used to extracted Sr from solution. Samples were separated using a ion exchange resin beds with 2.5M HCL as the eluting agent. For full details are see Appendix I.

Preparation of foraminiferal samples

Between four and six foraminifera were used for Sr analysis. Approximately 1 ml of dissolved sample was loaded on preconditioned ion exchange column to remove the Sr fraction.

Water samples were loaded on single tantalum filaments prepared with 1M phosphoric acid. Foraminifera were loaded on rhenium filaments with a TaF activator. Isotope ratios were measured on a Finnegan 262 mass spectrometer run in multidynamic mode. Measured ratios were corrected for fractionation relative to $^{87}Sr/^{86}Sr$ = 0.1194 and normalised to a value of 0.710248 for the NBS 987 Sr isotope standard. Eight determinations of North Atlantic Seawater yield a mean value of 0.709175 ± 0.000016 (2 sigma)

4.7 Sequential leaching and REE

A four stage sequential leach method was adapted from Tessier *et al.* (1979). See Appendix I for detailed procedure. The leaches from stages 1 to 3 were analysed for major and minor elemental analysis on a Perkin Elmer Optima 3300RL Inductively Coupled Plasma Atomatic Emission Spectrometer (ICP-AES) (Royal Holloway College, University of London, NERC facility). REE (stages 3 and 4) were analysed on a Quadrupole Inductively Coupled Plasma-Mass spectrometer (ICP-MS). Analysis was conducted at Kingston University NERC facility. REE concentrations were normalized to a chondritic meteorite (Boynton, 1984).

4.8 Biogenic silica

$BSiO_2$ was determined by the wet sediment leach technique (Dobbie, 1988).

Sample preparation

1. Less than a gram of sediment was placed in plastic vial and dried at 40°C.
2. 50 mg of dried sediment was digested in 20 ml of 2M sodium carbonate solution in a water bath at 90 - 100°C for 4 hours.
3. The cooled samples were then filtered through a Whaterman542 hardened ash less filter paper to remove any undigested sample. The sample was filtered into a 100ml plastic volumetric flask and the filtrate was made up to 100ml using de-ionised water.

Sample analysis

Samples were analysed for Al and Si on a Perkin Elmer Elan 6100 DRC plus Mass Spec in standard mode. Three standards (100, 250, 500 and 1000ppb Al and SiO_2) were used to produce a linear calibration graph. Values were corrected for nonamorphous silica derived from clays by deducting twice the Al_2O_3 content of the solution, assuming the SiO_2/Al_2O_3 ratio of clays in this region to be approximately two.

4.9 Tephrochronology

Shard extraction and identification

Cores were sub sampled at 1 or 2 cm intervals across the Younger Dryas chronozone. Tephra was extracted following the standard specific density separation technique for rhyolitic shard extraction (Turney, 1998). Tephra shard identification was based on characteristics (shard morphology, vesicularity and isothoprism differences under plane polarised light) identified by Perrson (1971). Rhyolitic shards are transparent or a light purple-pink colour, their morphological relief is low and the Becke line moves out from the shard when the focus is altered with the microscope.

Chapter 5

Pilot study

5.1 Introduction

In Chapter 2, six combinations of proxies were proposed as alternative palaeosalinity and geochronological indicators for isolation basin sediments. As only $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ had previously been applied to isolation basin sediments, a number of these proxies underwent a degree of preliminary testing before any larger studies were undertaken. This chapter presents the results of pilot studies conducted with $\delta^{13}C_{org}$ and C/N ratios, $\delta^{18}O_{diatom}$, $^{87}Sr/^{86}Sr$, sequential leaching of major, trace, rare-earth elements and tephrochronology. The nature and size of the individual pilot studies undertaken for each proxy varied depending on previous research of the technique.

5.2 $\delta^{13}C_{org}$ and C/N ratios

This pilot study aimed to establish if $\delta^{13}C_{org}$ and C/N ratios could distinguish between marine and freshwater sediment. Marine sediment is expected to be around 8‰ higher and have C/N ratios >12 compared to freshwater sediment (Boutton, 1991).

5.2.1 Results

In total, 32 samples were analysed for $\delta^{13}C_{org}$ and C/N ratios from Upper Loch nan Eala (ULNE) (Figure 3.2). This sampling interval was broad enough to ensure that samples were taken from marine and freshwater sections of the ensure that samples were taken from marine and freshwater sections of the core. The two cores were cross-correlated by matching key minerogenic and limnic lithostratigraphic boundaries between the cores. For a summary of the RSL history of this site, see Chapter 3 section 3.2.7. Figure 5.1 shows the $\delta^{13}C_{org}$ and C/N ratios from the Russian core collected with the summary, diagram of the diatom flora by Shennan *et al.* (1994). The $\delta^{13}C_{org}$ and C/N data show a clear correlation with the diatom salinity reconstruction (Shennan *et al.*, 1994). Based upon sediment lithostratigraphy and the diatom summary ULNE, has been divided into three zones.

Zone 1

The $\delta^{13}C_{org}$ values through this zone are relatively high –19‰ and –17‰ with relatively low C/N ratios, 10 to 13. The diatom flora is dominated by polyhalobous and mesohalobous forms; the diatom flora from the previously collected core suggest full marine conditions (Shennan *et al.*, 1994).

Zone 2

The $\delta^{13}C_{org}$ values decrease through this zone; the values range from –26‰ to –23‰, while C/N ratios increase from 11 to 16. The values from 493 cm and 545 cm appear to be clear outliers because they do not follow the general trend. The diatom flora is dominated by oligohalobous (80%), and halophobous forms. The diatom assemblage suggests from the previously collected core completely freshwater conditions (Shennan *et al.*, 1994).

Zone 3

The $\delta^{13}C_{org}$ values become steadily more enriched throughout this zone from –21‰ to –17‰, C/N ratios decrease from 14 to 11. This zone has comparable $\delta^{13}C$ and C/N values to Zone 1. The diatom flora is composed of a mixed assemblage of polyhalobian, mesohalobian, oligohalobous and halophobous forms, but polyhalobous and mesohalobous became increasing dominant through the zone (between 60 and 80%), which suggests the environment became more saline through the zone and changed from a brackish/marine to a marine basin (Shennan *et al.*, 1994).

5.2.2 Discussion and conclusion

The marine section of the core is characterised by high $\delta^{13}C_{org}$ values (–20‰ to –18‰) and lower C/N ratios (10 to 13) compared to freshwater sediment in isolation basins (–20‰ to –26‰ and 13 to 16). Based on the diatom reconstruction by Shennan *et al.* (1994) Zone 1 and 3 are marine environments and Zone 2 is a freshwater loch. The data shows there is approximately an 8‰ difference in $\delta^{13}C_{org}$ values between the fully marine and freshwater loch environments from the Russian core analysed. The $\delta^{13}C_{org}$ values record intermediate values (–23‰ to –21‰) between 521 cm to 457 cm. The diatoms summary at the base of Zone 3 is characterised by a peak in the species *Paralia sulcata,* which is characterised as a polyhalobian species (fully marine) (Shennan *et al.*, 1994). However, this species has been suggested to be indicative of brackish water (mesohobous) conditions (Zong, 1997).

The pilot study has established that $\delta^{13}C_{org}$ and C/N ratios can distinguish between marine and freshwater sediment. The results may even imply $\delta^{13}C_{org}$ can potentially characterise the brackish phase. This study highlights the potential of $\delta^{13}C_{org}$ and C/N ratios from isolation basin sediments as proxies that could reconstruct relative trends in palaeosalinity. The positive results of this pilot study led to a larger investigation of $\delta^{13}C_{org}$ and C/N ratios as a palaeosalinity proxy within isolation basins (Chapter 6). This recognises that this small pilot study has some significant limitations, for example, the possible effects of palaeoclimate on $\delta^{13}C_{org}$ values especially during the Lateglacial and lack of contemporary data to calibrate the marine and freshwater zones identified. These issues are addressed in the larger study.

5.3 Oxygen and carbon analysis of foraminifera

As Lloyd and Evans (2002) had previously demonstrated, the potential of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ from the species, *H. germanica*, as a palaeosalinity proxy within isolation basins, a pilot study to test if $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ could distinguish between marine and brackish environments, was not necessary. However, a pilot study was conducted to establish which of the field sites was the most suitable for analysis. The three field sites ULNE, the Holocene section of Rumach VI and Loch Nan Corr (LNC) (Figure 3.2, 3.20) were thought to have relatively high abundance of foraminifera due to observations made at the time of core extraction in the field and previous research at Rumach VI and LNC (Lloyd, 2000; Lloyd and Evans, 2002).

5.3.1 Results

Table 5.1 presents the results of the foraminiferal counts from each fossil isolation basin. The results show that the new piston core from ULNE is devoid of foraminifera. Rumach VI contains *H.germanica* species at three levels within the piston core 900, 750 and 400 cm. These samples cross the boundary between fully marine and brackish conditions within the core according to the foraminiferal summary diagram (Figure 3.15b) (Lloyd and Evans, 2002). LNC contains the highest abundance of *H.germanica* through the core between 700-500 cm. The foraminifera samples from LNC cross the boundary between fully marine, brackish conditions within the basin Figure 3.22 (Lloyd, 2000).

5.3.2 Discussion and Conclusion

LNC was chosen as the field site to apply $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ of because the highest abundance of H.germanica species occur across key lithostratigraphic boundaries of the core. Analysing this site for $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ would produce a detailed picture of how the proxy relates to salinity because it contains additional data about organic carbon source from the $\delta^{13}C_{org}$ and C/N ratios.

5.4 Oxygen analysis of diatoms

Ideally, a study similar to $\delta^{13}C_{org}$ and C/N ratio pilot study would have been undertaken to establish if marine and freshwater diatoms were isotopically different from one another. However, due to the need for the development of an extraction technique suitable for extracting over 10μg of pure diatoms across the range of sediment facies found within isolation basin sediments, a only a pilot study to establish which field sites are the most suitable application of the technique, was undertaken. In order for $\delta^{18}O_{diatom}$ to have the best opportunity of success, a fossil isolation basin with high diatom abundance throughout its sequence was required. In order to test the technique as a palaeosalinity proxy the method should be capable of reconstructing salinity on all types of isolation sequences including, rapidly and slowly isolated basins. Therefore, ULNE, Main Loch Nan Eala (MLNE) and the Holocene section of Rumach VI were chosen for examination. Based upon previous research ULNE, MLNE and Rumach VI were known to contain high diatom abundance (Figure 3.2) (Shennan *et al.*, 1994, 1999) but, LNC, based on previously unpublished data, is known to have low diatoms abundances.

5.4.1 Method

The three sites were sub sampled at 100 cm intervals for diatom analysis from the top to the bottom of the cores to establish the degree of diatom variability throughout each of field sites. An equal amount of material was pipetted onto slides and the total number of diatoms per slide were counted.

5.4.2 Results

Tables 5.2 to 5.4 present the results of the diatom counts from ULNE, MLNE and Rumach VI and show the results of total diatom abundance variability in each core. ULNE had the highest diatom abundance and least diatom variability throughout the sequence. In contrast Rumach VI had the lowest diatom abundance and least diatom variability throughout.

5.4.3 Discussion and conclusion

ULNE was picked as the site for $\delta^{18}O_{diatoms}$ analysis. Material from a Russian core was used to develop the extraction technique upon (see Chapter 4 for description).

5.5 Strontium

Strontium analysis is an expensive analytical technique and limited access to instrument time limits the number of samples that can be analysed. Therefore, it was vital to establish if a $^{87}Sr/^{86}Sr$ signal could distinguish between the marine and non-marine signal in the Arisaig area (Figure 3.2).

5.5.1 Methods and materials

Water samples were collected from within Rumach Tidal Pond (RTP), seaward of the sill and the two stream inputs of the basin (Figure 3.18), in order to construct a salinity mixing line. Ideally, a brackish water sample should have been collected. Unfortunately, it was not possible to collect such a sample in the Arisaig area. It is assumed that RTP experiences the same Sr hydrological regimes as Rumach VI as they are less than 0.25 km apart (Figure 3.2).

The Holocene section of Rumach VI was sub sampled for foraminifera (Figure 3.2 and 3.16b), but only three intervals contained sufficient material for analysis: 412 cm, 764 cm and 892 cm (see Table 5.1). The published salinity reconstruction from the Holocene section of Rumach VI is shown in Figure 3.15b. The foraminiferal reconstruction suggests a gradual reduction in salinity up core (Lloyd and Evans, 2002).

5.5.2 Results

The results of Sr analyses and salinity data are given in Table 5.5. The salinity of RTP was uniform from low tide to high tide between the basin and outside the sill. This suggests the basin was fully mixed with Atlantic seawater. The marine water inside and outside RTP are concordant with the Sr values of the Modern Seawater standard (MSS) which clusters around 0.709175 (McArthur, 1994). The two freshwater streams that flowed into the back of the basin appeared not to influence the salinity of the basin as the salinity of Loch nan Ceall is identical to RTP. Nevertheless, the freshwater streams are significantly more radiogenic than the basin water. The contrasting $^{87}Sr/^{86}Sr$ compositions meant a $^{87}Sr/^{86}Sr$ salinity mixing could be constructed for RTP. Figure 5.2 shows $^{87}Sr/^{86}Sr$ plotted against salinity. The mixing line was then used to extrapolate the palaeosalinity of the three foraminiferal samples. The two samples at 892 and 764 cm are within the accepted range of MSS. However, the sample at 412 cm is significantly more radiogenic than the other two samples. When the palaeosalinity values are extrapolated from the mixing line, there is only a 0.5 psu difference between the 892 cm, 764 cm and 412 cm.

5.5.3 Discussion

The aim is to make quantitative reconstructions of palaeosalinity from a mixing line (Figure 5.2). Previous research by Lloyd and Evans (2002) have related groups of foraminiferal assemblages within Scottish isolation basins to basin water salinity and sill altitude. The quantitative $^{87}Sr/^{86}Sr$ reconstructions from Rumach VI samples can be compared with the foraminiferal salinity associations. The faunal reconstruction (Figure 3.16b) suggests that the samples 892 cm and 764 cm were deposited in marine waters due to the dominance of a number of nearshore self species, e.g. *Elphidium excavatum, Nonion depressulus* as well as the brackish lagoon taxa and *H. germanica* (Lloyd and Evans, 2002). The association of *N. depressulus* and *E. excavatum* are indicative of a fully marine environment, *H. germanica* and *Nonion depressulus* are thought to have a relative salinity between 33.5 to 37.8 psu (Lloyd and Evans, 2002). The $^{87}Sr/^{86}Sr$ salinity reconstruction suggests the salinity was around 33psu (Figure 5.2) which is in agreement with the faunal data (Lloyd and Evans, 2002). The sample at 412 cm also agrees with the faunal reconstruction (Figure 3.16b), which suggests the environment is relatively less saline (represented by the dominance of species *H. germanica*, *Ephidium williamsoni* and the saltmarsh taxa *Milammina fusca*) compared to the fauna of samples 892 cm and 764 cm. Based on contemporary foraminifera data of Lloyd and Evans (2002) this sample fits most closely with an association that has a salinity reconstruction at 31.5 ± 5 psu (association of ME, *M.fusca* and *E. williamsoni* of Lloyd and Evans, 2002). This association of species is thought to have a relative salinity of 31.5psu (Lloyd and Evans). The ^{87}Sr/^{86}Sr mixing lines suggest that sample 412 cm has a salinity of 32.5 psu (Figure 5.2) which is in broad agreement with the faunal data. The faunal data further suggests that 412 cm was the most saline point within the brackish section of the core (Lloyd and Evans, 2002). This could explain the small salinity range (0.5 psu) between the three samples.

There are significant limitations of with this study, the most obvious being the lack data from a range of contemporary brackish isolation basins within Arisaig. This would test if the mixing line for Sr is linear for the Arisaig area. It is possible that the mixing line would be more hyperbolic in form. Data from estuarine studies are largely hyperbolic (e.g. Ingram & DePaolo, 1993; Reinhardt *et al.*, 1998a). In addition, analysis of modern foraminifera from a range of brackish environments would also independently test the accuracy of the mixing line constructed from water samples.

5.5.4 Conclusion

A ^{87}Sr/^{86}Sr salinity mixing line for the Arisaig area, between marine and freshwater end members, from which quantitative estimates of palaeosalinities were made from Rumach VI. The palaeosalinity reconstruction from ^{87}Sr/^{86}Sr is in agreement with the other independent faunal data from the site. This preliminary study highlights the potential of ^{87}Sr/^{86}Sr to produce quantitative palaeosalinity reconstructions from isolation basin sediments. This type of reconstruction is not possible when using stable isotope and ecological techniques at present. $^{87}Sr/^{86}Sr$ is able to determine the impact of salinity on isolation basins independent of changes in temperature, oxygen content and pH. The application of $^{87}Sr/^{86}Sr$ has enormous potential for Lateglacial sea-level reconstructions where temperature might affect the palaeosalinity reconstruction of stable isotope proxies.

5.6 Sequential leaching

Due to problems of element mobility, a pilot study was conducted to see if sequential leached sediment from isolation basins could distinguish between marine and freshwater sediment. If elemental concentrations are related to salinity, the elements Na, Mg, Ca, Cl, K, Sr, S, and Li will be found in higher concentrations in marine compared to freshwater sediment. If anoxic conditions occurred around the isolation contact, the trace elements As, Ba, Cd, Cu, Co, Mo, Mn, Ni, Pb, U, Zn and V will peak. Also the REE Ce and Eu should only display positive or negative anomalous values in marine sediment.

5.6.1. Results

Figures 5.3 shows a summary of all the elemental profiles against the biological salinity reconstruction from ULNE (Shennan *et al.*, 1994). Zone 1 and 3 represent marine conditions while Zone 2 represents sedimentation from a freshwater environment. Only the elements Ba, Cd, Co, k, Mg, Mn, Ni, V, Y and Zn could be reliably analysed.

Major elements

The only major element that has higher elemental ratios in the marine compared to the freshwater zones is Mg. The only other two major elements analysed were Sr and K, neither element had higher ratios in the freshwater compared to the marine phases.

Trace elements

A number of trace elements peak around the higher and lower isolation contacts: Mn, Ni, V, Zn and Y peak around the contacts. While both Zn and Y peaked around the contact, they also display higher ratios through the freshwater section of the core compared to the two marine sections. The trace elements Ba and Cd had breaks in analysis around each contact.

Rare Earth Elements

Figure 5.4 show that the fresh and marine samples have different absolute concentrations. The three freshwater samples taken from the depths 616, 632 and 664 cm have higher absolute concentrations than the marine sample but all the freshwater samples exhibit negative Ce_{anom} and Eu_{anom} patterns. In contrast, the marine samples taken from the depths 712, 728, 760 and 776cm do not display any anomalous patterns for Ce or Eu.

5.6.3 Discussion and conclusion

The major elemental data is limited but appears to show a poor relationship with salinity, this could be attributed to elemental mobility since deposition. A number of trace elements do peak around the two isolation contacts suggesting anoxic conditions may have occurred at these two points in the core. While the REE elements show two distinct grouping, REE patterns show the opposite of the expected trend and appear not to be related to palaeosalinity. It is possible that REE are reflecting their original formation environment. Another possibility is that elements were remobilised, since under strongly reducing or acidic condition, REE can be diagenetically dissolved and diffused back into the water column (Elderfield and Sholkovitz, 1987). Thin acidic peaty soils prevail in ULNE catchment which could have caused element mobilised.

This study suggests major and REE elements are not a reliable indicator of palaeosalinity within fossil isolation basin sediments. REE cannot allude to the depositional setting of isolation basin sediments. Even though the trace elements might reflect anoxic conditions associated with the isolation process and the REE show a difference in absolute concentration between marine and freshwater samples. Elemental analysis was not used further in this thesis because other proxies such as $\delta^{13}C_{org}$ and C/N ratios produced more reliable results and the preparation of $\delta^{13}C_{org}$ and C/N ratios is less time consuming especially when multiple cores are to be analysed.

5.7 Tephrochronology

The dispersal pattern of tephra shards is highly variable across a region and especially within a single basin where concentrations can be vary significantly different within a few meters (Davies *et al.,* 2001; Mackie *et al.,* 2002; Pyne-O'Donnell, 2004). For example, within a basin, a core can record a macrotephra deposit and only a few meters away a core from the equivalent depth will not contain a macrotephra layer (Davies *et al.,* 2001). Due to the effect of tidal scouring, it is unknown if micro-tephra layers will be preserved within marine/brackish isolation basin sediments. Accordingly, a pilot study was undertaken to establish if the Vedde Ash tephra had been deposited in isolation basin sediments within Arisaig.

5.7.1 Method and materials

A number of basins, where the Younger Dryas chronozone is thought to have occurred in the freshwater section of the core, were analysed for Vedde Ash. It is thought that tephra will be preserved in higher abundance in the freshwater sediment because freshwater environments are lower energy environments compared to fully marine phases.

The three field sites in Arisaig with lacustrine Younger Dryas sediment: LTB, TB, LAM were sub samples at 1 to 2 cm intervals across the Younger Dryas section of the core. As TB had the clearest evidence of the Younger Dryas event, sediment cores were also analysed from the back and middle of the basin. This would identify if tephra dispersion and preservation is influenced by the basin hydrodynamics, for example, tidal scouring may be less at the back of a basin compared to the middle. ULNE and MLNE were also sampled because the radiocarbon dating (Shennan *et al.*, 1994) suggested that the Younger Dryas occurred around their lower isolation contacts (Shennan *et al.*, 2000). ULNE and MLNE were also sub sampled at 1 cm intervals across the isolation contact.

5.7.2 Results

From ULNE, six shard like fragments were identified under the polarising microscope. However, the abundance was thought too low for electron probe microanalysis and therefore the presence of tephra shards cannot be confirmed. Unfortunately no rhyolitic tephra shards were identified from LTB, TB, LAM or MLNE.

5.7.3 Discussion and conclusion

The lack of tephra in the three lacustrine deposits suggested that the Vedde Ash tephra layer is not well preserved in the Arisaig area. It is speculated that the effects of tidal scouring prevented tephra settling out of the water column, or the air fall of the ash deposit was low over this area compared to other areas across Scotland. The basin size and number of inflows has been shown to influence tephra preservation. The larger the catchment size and greater the number of stream inflows to a lake help to funnel the tephra into a lake (Pyne-O'Donnell, 2004). LTB, TB and LAM have smaller catchments than ULNE, which may have influenced shard concentration. The poor results from this pilot study meant no further tephra analysis was carried out.

5.8 Summary

The pilot studies have shown:

1. $\delta^{13}C_{org}$ and C/N ratio are suitable techniques as potential palaeosalinity indicators from isolation basin sediments.

2. The pilot study undertaken for the $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ and $\delta^{18}O_{diatom}$ established the field sites upon which these proxies should be tested.

3. Preliminary results suggest $^{87}Sr/^{86}Sr$ has the potential to make quantitative reconstructions of palaeosalinity within isolation basin sediments for the first time. Unfortunately, $^{87}Sr/^{86}Sr$ could not be extended to a more detailed study because insufficient foraminiferal material existed within sediment sequences from the Arisaig field area.

4. The sequential leached major, trace and REE elements do not appear to be related to palaeosalinity changes within isolation basins sediments and therefore will not be used further in this thesis.

5. The Vedde Ash tephra layer appears not to be preserved within Arisaig isolation basins sediments. The method will not be applied further in this thesis.

Chapter 6

Carbon isotope and C/N ratios from bulk sediment as a palaeosalinity proxy for isolation basin sediments

6.1 Introduction

The primary aim of this thesis is to find alternative methods of reconstructing salinity trends within Scottish isolation basin sediments to reconstruct RSL change. The potential for $\delta^{13}C_{org}$ and C/N ratios to distinguish between marine and freshwater sediment was discussed in Chapter 2. Following the positive results of the pilot study (see Chapter 5), a larger study was conducted to build upon the limitations of the pilot study. This Chapter presents the results of $\delta^{13}C_{org}$ and C/N ratio measurements from a range of contemporary isolation basins and multiple fossil isolation basin sediments that vary in age from Lateglacial to late Holocene, in Arisaig and Kintail (Figure 3.1, 3.2, site map). These sites were chosen in order to test the proxies over the full range of isolation basin types and test the applicability of the method to areas other than Arisaig.

Chapter 2 showed that typically marine organic matter has higher $\delta^{13}C_{org}$ values (around –22‰ to –17‰) and lower C/N ratios (<12) compared to most terrestrial and freshwater organic material (–30‰ to –25‰, C/N ratios >12) (Boutton, 1991). These two methods can be used in tandem to identify the source (autochthonous and allochthonous) of organic material preserved within sediment matter (Leng and Marshall, 2004) (e.g. Thornton and McManus, 1994; Yamamuro, 2000).

6.2 Research aims

The aim is to test $\delta^{13}C_{org}$ and C/N ratios as an alternative proxy to biological indicators for palaeosalinity within isolation basin sediments. The two proxies will identify the source of organic material preserved (marine vs. terrestrial) in isolation basins and can be used to indirectly identify trends in palaeosalinity. Modern plants and surface sediments in and around modern freshwater, brackish and marine isolation basins in Northwest Scotland were sampled in order to obtain a calibration data set of $\delta^{13}C$ and C/N ratios. Data from the contemporary materials are compared to results of bulk organic data from Lateglacial and Holocene aged isolation basin sediments. Across the Lateglacial transition $\delta^{13}C_{org}$ and C/N ratios are influenced by other factors such as temperature and CO_2 variation, in addition to salinity.

6.3 Results

6.3.1. Contemporary data

$\delta^{13}C$ and C/N ratios from modern plant material

Surface sediment samples and plant material were taken from within and around three sites; Rumach Tidal Pond (RTP) in Arisaig, Loch nan Corr (LNC) in Kintail and Craiglin Lagoon in Knapdale (Figure 3.1, 3.2 3.18, 3.21 3.24). A biplot of C/N vs. $\delta^{13}C_{org}$ (Figure 6.1a) from the modern plant data (Table 6.1) shows the data group into two distinct fields, controlled by differences in $\delta^{13}C_{org}$ values. Terrestrial and freshwater plants have $\delta^{13}C_{org}$ values between –32.5‰ and –24.9‰, while marine aquatics range from –21.7‰ to –17.3‰ (Table 6.1). The C/N ratios of the contemporary dataset do not display any real partitioning, as there is a large degree of overlap between the terrestrial, freshwater aquatics and marine organic materials. The terrestrial and freshwater plants have C/N ratios from 10 to 97, while the marine aquatic plants range from 7 to 41.The bulk surface sediments from the contemporary basins fall within the fields of data (marine/terrestrial and freshwater aquatics) defined by the modern plant samples. The marine bulk surface sediment from RTP plots within the field of data defined by the marine plants and similarly for the freshwater bulk surface sediments (Figure 6.1a). All of the terrestrial and freshwater plants have $\delta^{13}C_{org}$ values that fall within the range for C3 plant types (see Chapter 2). The low C/N ratios (<20) in some of the terrestrial plants are common in non-woody shrubs and herbs (Meyer and Ishiwatari, 1993). Unfortunately, due to sampling problems, contemporary marine, brackish or freshwater plankton could not be collected from any of the field sites.

The four bulk freshwater surface sediment samples from the basins of LNC (modern freshwater basin Stage 4, Figure 1.1) and the freshwater stream inputs into RTP and Craiglin have C/N ratios of 14.4, 14.6 and 16.6 and $\delta^{13}C_{org}$ values, –29.4‰, –29.3‰ and –28.4‰ while the bulk marine sediment from RTP (modern marine basin Stage 2, Figure 1.1) has a C/N ratio of 7.7 and $\delta^{13}C_{org}$ value of –20.8‰. These values are typical of the modern marine plants, although the low C/N ratio perhaps suggests that marine plankton (C/N range typically 4-10) or a sea weed such as *Cladoptom rupestris* (C/N = 8.2) is predominant. Interestingly, the single sediment sample from RTP has $\delta^{13}C_{org}$ and C/N values which seem to suggest that the marine isolation basins contain a limited organic input from terrestrial sources. The bulk surface sediment sample was collected from the deepest part of Craiglin Lagoon (station 2, see Figure 3.24) (the brackish/marine basin Stage 3 Figure 1.1) and has a C/N ratio of 9.3 and $\delta^{13}C_{org}$ value of –18.5‰.

The surface sediment sample from Craiglin Lagoon sits within the field defined by modern marine aquatic data. The stream sample from this basin falls within the overlapping terrestrial plant and freshwater aquatics fields (Figure 6.1a). The carbon isotope and C/N ratio of the bulk sediment sample from the basin suggests that the majority of the organic input to this basin is from the marine environment, despite the surface waters being heavily influenced by freshwater (surface water salinity ~15 psu see Figure 3.26 salinity plot). The basin is stratified between stations 1 to 3 (Figure 3.24) and, in the deepest part of the basin bottom salinity is >30 psu (i.e. station 2, where the surface sample was taken), near fully marine values. A spot diatom count from the centre of the basin is composed of polyhalobous (marine) and some mesohalobous forms (brackish); the assemblage being dominated by *Paralia sulcuta, Cocconies scutellia* and *Rhabdonema minutum* species (Appendix II). This shows that the flora of the basin is influenced by bottom water salinity and it is likely that the marine aquatics contribute to the bulk organic signal, as the C/N ratio is similar to marine aquatic from RTP. Overall, Craiglin Lagoon appears to receive limited organic input from terrestrial sources despite the heavily forested catchment and multiple ephemeral streams.

The contemporary data from Northwest Scotland is limited, for example, contemporary diatoms were not in sufficient abundance to easily harvest and only one sample was analysed from the brackish phase. Contemporary measurements from the literature have been used to create more comprehensive fields of $\delta^{13}C_{org}$ and C/N ratio data for the marine, brackish and freshwater environments (Table 6.1b, Table 6.2). Figure 6.1b was constructed using the contemporary data from NW Scotland plus data from the published literature that had both $\delta^{13}C_{org}$ and C/N ratios for each sample. The brackish field includes data from coastal lagoons, subtidal estuaries and saltmarsh surface sediments. Based on the data collected from Northwest Scotland and published data sets, marine samples will fall within a field between –17‰ and –22‰ with C/N ratios <12; freshwater samples lie between –24‰ to –30‰ with C/N ratios >12 and brackish values overlap between the two fields (Table 6.2).

6.3.2 Sediment cores

In total, eight fossil isolation basins were examined from Arisaig (Upper Loch nan Eala, Maine Loch nan Eala, Rumach VI, Upper Allt Dail An Dubh-Asaid, Torr a'Bheithe, Loch Torr a' Bheithe and Loch a' Mhuilinn) (Figure 3.2) and

Kintail (Loch nan Corr) (Figure 3.20). Five sediment cores from Upper Loch nan Eala, Maine Loch nan Eala, Rumach VI (2 cores) and Loch nan Corr are presented first, as they were examined in the greatest detail (Figures 3.11,3.13, 3.15a,b and 3.22). This is followed by four Lateglacial sediment cores Upper Allt Dail An Dubh-Asaid, Torr a'Bheithe, Loch Torr a' Bheithe and Loch a' Mhuilinn which were examined in less detail (Figure 3.3, 3.6, 3.8 and 3.10). The sediment data is discussed in relation to the contemporary data collected for this research and the published data sets defined in Figures 6.1b.

Upper Loch Nan Eala

ULNE records RSL change from the Lateglacial (12.4 ka cal BP) through to the late Holocene (Shennan *et al.,* 1994, 1995) (Figure 6.2). Overall, changes in the isotope data are similar to the general trend in the biological salinity reconstruction (Figure 6.2). The core has been divided up into eight zones. The new core from ULNE is longer than the original core collected and analysed by Shennan *et al.* (1994). Therefore the transitional sequence across each isolation contact appears more extended than the original core (Shennan *et al.*, 1994). Based on core lithology and diatoms spot counts the two cores have been correlated. The main isolation contacts, between Zones 1 and 2 and Zones 7 and 8, are placed between 647 to 645 cm and 180 to 172 cm based upon diatom spot counts and lithostratigraphic analysis (Appendix II). The transition from Zone 2 to 3 is based upon a peak in *Paralia sulcuta* species, beginning at 535 cm (Appendix II). Based upon lithostratigraphic analysis, the base of Zone 5 (236 cm) corresponds to 290 cm from the published core.

Zone 1 – Lateglacial marine

Zone 1 is defined by relatively high $\delta^{13}C_{org}$ values and low C/N ratios (Figure 6.2). The transition to Zone 2 correlates very clearly with a drop in polyhalobian diatoms replaced by oligohalobous diatoms. Based on the contemporary data and published results (Figure 6.3, Table 6.2), organic material from Zone 1 is probably largely derived from marine algae and is within the range of organic material from marine diatoms (Prahl *et al.,* 1980). Climate change, during the Lateglacial, may have had an influence on the $\delta^{13}C_{org}$ values but this cannot be identified from the data. The correlation between the isotope data and the trends in the biological data (Figure 6.2), around the marine transition, suggest that the level of marine inundation of the basin, represented by reconstructed salinity, is a major factor controlling the source of organic material and therefore the $\delta^{13}C_{org}$ and C/N values across the Zone 1 to 2 boundary. Climate changes associated with the Lateglacial are most likely to have had an influence on $\delta^{13}C_{org}$ in Zone 1, since this represents sediments deposited before 12.4 ka cal yrs BP i.e. the Lateglacial Interstadial. Numerous lake sequences across Europe (e.g. Hammarlund, 1993; Turney, 1999; Nuñez *et al.*, 2002) record isotopically higher $\delta^{13}C_{org}$ values during the Lateglacial. However, $\delta^{13}C_{org}$ values from Zone 1 (Lateglacial marine) from ULNE overlap with values from Zone 4 (mid Holocene marine phase); there is no clear climate change signal between the Lateglacial and Holocene marine sediments. The samples from Zone 1 form a relatively well-defined field in Figure 6.3, having a range of $\delta^{13}C_{org}$ values from –21.0‰ to –16.5‰ but fairly consistent C/N values.

Zone 2 –Freshwater loch

Zone 2 is characterised by relatively low $\delta^{13}C_{org}$ values and high C/N ratios. There is an increase in %TOC (from 4% to 18%) between Zones 1 and 2, due to an increase in productivity within the basin associated with the change in aquatic environment. Climate changes associated with the Younger Dyras chronozone (12.6 to 11.4 ka cal BP, Walker *et al.,* 2003) are most likely to have had an influence on $\delta^{13}C_{org}$ in Zone 2, since this represents sediments deposited younger 12.4 ka cal yrs BP. A number of lake records across Europe (e.g. Turney, 1999; Nuñez *et al.*, 2002) record isotopically higher $\delta^{13}C_{org}$ values during the Younger Dryas. In Zone 2, the bulk organic material has lower $\delta^{13}C_{org}$ values and the data largely plots within overlapping brackish, freshwater aquatic and terrestrial fields defined by the contemporary data set (Figure 6.3). This reflects the transition in values from the marine to freshwater environment.

Three of the values over the transition, between Zone 1 and Zone 2, have higher $\delta^{13}C$ values (–21.5‰ to –21.2‰) that actually plot in the marine field. Despite the overlap with the brackish field (Figure 6.3), the samples from Zone 2 are thought to indicate a freshwater environment. The generally low C/N ratios suggest that the majority of the organic material originated from aquatic plants, although terrestrial plant material cannot be excluded. Overall, the data does not suggest there is a clear Younger Dryas event in the ULNE sediment.

Figure 6.2 shows a gradual increase in the C/N ratio through Zone 2 suggesting an increase in the contribution from terrestrial plants or a change in the dominant plant type. The single excursion to a C/N value of 25 and corresponding slight decrease in $\delta^{13}C_{org,}$ is probably due to a large fragment from a terrestrial plant within the sample and confirms some terrestrial contribution. The increase in terrestrial plant material input to the basin at this time, could be due to a greater development of the catchment vegetation associated with climate amelioration over the transition from Younger Dryas to Holocene. Samples from Zone 2 form a well defined field, with only a minor overlap with the other freshwater Zones 5 and 7 and brackish Zone 3 (Figure 6.3). In general, $\delta^{13}C_{org}$ values in Zone 2 are 1-2‰ higher than the other freshwater Zones. There is also a corresponding increase in the C/N ratios from 13 to 20 through the freshwater sequences (Figure 6.2). These differences may be associated with changes in the types of organic material (planktonic, aquatic macrophytes and terrestrial plants) associated with changes in water depth in the basin through the Holocene. Water depth can have an important role in determining the type of aquatic plants within a basin. The data suggest, that when the sediments of Zone 2 were formed the basin was a relatively deep freshwater loch, with organic material predominantly from plankton and aquatic plants, and with only minor inputs of terrestrial organic material. By the time sediments forming Zone 7 were deposited, 400 cm of sediment had accumulated, and the basin would have been a significantly shallower freshwater loch, with a larger fringe of marginal (both macrophytes and terrestrial) plants.

Zone 3 – brackish basin

Zone 3 is characterised by a decrease in $\delta^{13}C_{org}$ values to between –22.6‰ and –22‰. Zone 3 correlates with the section of the published core characterised by a return of marine diatoms. Significantly, a section of the core dominated by one species *Paralia sulcata*, is characterised as a polyhalobian species (fully marine) but is suggested by Zong (1997) to be mesohalobous (brackish) because it is diagnostic of transitional (brackish) conditions immediately before or after isolation. This species reduces at 345 cm in the original core (Shennan *et al.,* 1994) and is replaced by diatoms representing more marine conditions. This transition in the original core has been correlated to 471 cm in the core used in this study (based on spot diatom counts).

Zone 3 shows a clear difference in $\delta^{13}C_{org}$ values from Zone 2 by approximately 3‰ over the transition, while the C/N ratio drops by ~3. Samples from Zone 3 form a well defined field in the C/N vs. $\delta^{13}C_{org}$ plot and sit at the boundary between the brackish and marine field defined by the contemporary data set (Figure 6.3). The intermediate $\delta^{13}C_{org}$ values (–22‰) of Zone 3 are clearly distinguishable from the previous marine (–18‰) and freshwater zones (>–25‰) (Figure 6.2). Intermediary $\delta^{13}C_{org}$ values, such as those of Zone 3, are typical of values from contemporary and core sediment from brackish environments, around –24‰ to –22‰ (Table 6.2) (Gearing, 1988; Voss and Struck, 1997; Westerman and Hendenstöm, 2002; Emeis *et al.,* 2003) and may indicate a mixture of plankton and aquatic plant materials from marine and freshwater environments. The relatively high C/N values in Zone 3 imply that organic material is composed of a mix of aquatic and terrestrial plant sources.

Zone 4 – Holocene marine

Within Zone 4 there is a trend towards higher $\delta^{13}C_{org}$ values (from –20‰ to –17‰) to a peak at around 342 cm and then decrease to around –19‰ at the top of the zone. The C/N ratios decrease over this zone from 14 to 12. This suggests an increase in the amount of marine organic material and a decrease in freshwater/terrestrial organic material. The high $\delta^{13}C_{org}$ values through Zone 4 (–17‰) could be interpreted as representing fully marine conditions similar to Zone 1 (–17‰) and certainly more marine than Zone 6 (–22‰) if the highest $\delta^{13}C_{org}$ value is considered "more marine". This is not supported by the diatom flora since both Zone 1 and 6 have substantially more marine diatoms than Zone 4. In addition, the sea-level curve based on a large number of sites in this area (Shennan *et al.*, 2000) shows higher RSL around 6 ka cal yrs BP (i.e. within Zone 6) (see Figure 1.4). The possible reason for the difference in $\delta^{13}C_{org}$ is changing types of marine aquatics or some other significant environmental variable (such as temperature change in Zone 1). The contemporary data from NW Scotland show that changes in marine aquatics can influence the $\delta^{13}C_{org}$ values for example, Craiglin Lagoon has a higher $\delta^{13}C_{org}$ value (–18.5‰) compared to RTP (–20.8‰) even though RTP is more saline (Table 6.1). These uncertainties highlight the problems of the methodology. While $\delta^{13}C_{org}$ and C/N data can clearly identify significant changes in organic material in *response* to changes in environment, they cannot identify the cause of the environmental change.

Zone 5 - Holocene freshwater loch

Zone 5 shows a clear difference in $\delta^{13}C_{org}$ and C/N ratios from Zone 4. The samples from Zone 5 have low $\delta^{13}C_{org}$ values and high C/N ratios and the data sits within the freshwater aquatic and terrestrial field, as defined by the contemporary data set (Figure 6.3). The generally high C/N ratios (14 to 24) suggest that the majority of the organic material originated from aquatic and terrestrial plants. There is an increase in TOC between Zone 4 and 5 (from 5% to 37%) associated with the change in aquatic environment. The isotope data correlate well with the trend in the biological data (Figure 6.2).

Zone 6 - Holocene marine

The $\delta^{13}C_{org}$ and C/N ratios from Zone 6 sit within the marine field (Figure 6.3). Within Zone 6 there is a trend towards decreasing $\delta^{13}C$ values (from –19‰ to –22‰) and increasing C/N ratios (from 10 to 12). This suggests a decrease in the amount of marine organic matter and an increase in freshwater aquatic and terrestrial organic matter, leading up to the final isolation of the basin at the transition between Zone 6 and Zone 7. The $\delta^{13}C_{org}$ are lower than marine Zone 1 and 4, despite Zone 6 containing a higher proportion of marine diatoms than Zone 1 and 4. The C/N ratios are stable. The $\delta^{13}C_{org}$ might suggest a trend, however, the $\delta^{13}C_{org}$ values plot within the marine field (Figure 6.3). In addition, the RSL curve shows that the mid-Holocene highstand in the RSL record occurs within Zone 6 (*c.* 6 ka cal yrs BP, Figure 1.4) (Shennan *et al.,* 2000). The difference between the $\delta^{13}C_{org}$ values between Zone 4 and Zone 6 is most likely due to changes in sources of organic material and highlights a problem of $\delta^{13}C_{org}$ and C/N data. Once within the marine realm, it is difficult to differentiate changes in RSL that may be recorded in the diatom flora.

Zone 7 – brackish transition environments

The samples from Zone 7 have the intermediate $\delta^{13}C_{org}$ values (–24 ‰ to –23.5‰) and high C/N ratio between 13 and 14. The data sits within the brackish field defined by the contemporary data set and suggest organic material is a mix of aquatic and terrestrial plants (Figure 6.3). These samples represent a transitional period of brackish conditions over the isolation contact before the final freshwater zone.

Zone 8- Holocene freshwater loch / infilled basin

The samples from Zone 8, have the lowest $\delta^{13}C_{org}$ values and high C/N ratios and the data sits within the freshwater field defined by the contemporary data set (Figure 6.3). The generally high C/N ratios (12 to 30), combined with the $\delta^{13}C_{org}$ data, suggest that the majority of the organic material originated from terrestrial plants (Table 6.2). The highest C/N ratios correlate with the transition from lacustrine to peat sedimentation in the core used in this study. The samples from Zone 7 have the highest C/N ratios, highest %TOC and lowest $\delta^{13}C_{org}$ compared to the freshwater Zones 2 and 5, suggesting that Zone 8 contains the largest terrestrial input, prior to the basin becoming completely infilled. Approximately 400 cm of sediment have accumulated between Zones 2 and 8 and the basin has become progressively shallower. As water depth decreased, a larger proportion of the basin would have come into the depth range of marginal aquatic plants, which therefore could have colonised a greater proportion of the basin and contributed a larger proportion of the organic material to the sediment. Also there would have been a corresponding reduction in the proportion of plankton to the biomass. This is partly supported by pollen/spore data which show substantial amounts of *Myriophyllum* (freshwater aquatic) and *Pediastrum* (green algal spore) in Zone 2, but these are relatively rare in Zone 5 and 7 (Shennan *et al.*, 1994).

Main Loch nan Eala

MLNE records a similar RSL history to ULNE (Shennan *et al.*, 1994). The isolation contacts are placed at 364-362 cm and 410-402 cm based upon diatom and lithostragraphic analysis (Appendix II). The new core is divided into three zones based upon the diatom reconstruction (Shennan *et al.*, 1994). The Holocene freshwater section of the core was unfortunately missing from the new core. A spot diatom count at the top of the core is dominated by *Paralia sulcata* (a species diagnostic of transitional conditions (Zong, 1997) confirming the new core stops near the top of the Holocene marine phase, identified by Shennan *et al.* (1994) (Appendix II). Overall, the isotope data follow the general trend in the biological salinity reconstruction (Figure 6.4).

Zone 1– Lateglacial marine

Zone 1 is characterised by fluctuating values in $\delta^{13}C_{org}$, C/N and TOC. The carbon isotopes range from –23‰ to –19‰, C/N ratios from 8 to 10 and TOC range from 0.6% to 2.7%. The data from Zone 1 plot, within the marine and brackish fields, reflecting the transition from Zone 1 to Zone 2 (Figure 6.5). Based on the contemporary data set and published results the organic material from Zone 1 is probably largely derived from marine aquatics and algae (Figure 6.5). The variations in $\delta^{13}C_{org}$ values between 458 cm to 428 cm may reflect the climate instability associated with the Younger Dryas chronozone. The peaks in C/N ratios and lower $\delta^{13}C_{org}$ values –23.1‰ are similar to those found in brackish environments and could be attributed to erosion of the catchment vegetation associated with climate deterioration of the Younger Dryas. The erosion of the terrestrial vegetation might have caused a marine and terrestrial organic material to mix, creating lighter $\delta^{13}C_{org}$ values. Nevertheless, the isotope data correlates with the trend in the biological data around the marine transition (Figure 6.4).

Zone 2 –Freshwater basin

There is an increase in TOC (from 9 to 13%) between Zone 1 and 2, possibly reflecting a reduction in clastic input to the basin or may be an increase in aquatic productivity associated with more freshwater input to the basin. The bulk organic material from the centre of the zone has low $\delta^{13}C_{org}$ (–25‰) and high C/N values (12). The isotope data plots within the brackish, freshwater aquatic and terrestrial fields defined in Figure 6.5. The overlap in values with brackish field represents the transition from Zone 1 to Zone 2. The samples from Zone 2 are thought to indicate a freshwater environment; the C/N ratios suggest the majority of the organic matter originated from aquatic plants, although terrestrial plant material cannot be excluded.

Zone 3 – Holocene marine

Zone 3 shows a clear difference in $\delta^{13}C_{org}$ and C/N ratios. Within Zone 3, there is a trend towards increased $\delta^{13}C_{org}$ values from (–21‰ to –18‰) to a peak at 164 cm and to a decrease to –19‰ at the top the core. The C/N ratios decrease over this zone from 12 to 10. This suggests an increase in the amount of marine organic material and a decrease in the amount freshwater/

terrestrial organic material. Interestingly, TOC increases at 164 cm from around 5% to 14% suggesting an increase in the aquatic productivity of the environment similar to either brackish or freshwater conditions. The diatom spot sample (144 cm) (Appendix II), at the top of the core is dominated by *Paralia sulcata*, species which is diagnostic of transitional conditions (Zong, 1997). This suggests that the TOC is indicating the transition to the isolation contact. Samples from Zone 3 form a well defined field in the C/N vs. $\delta^{13}C_{org}$ plot (Figure 6.5), with only a minor overlap with the other marine phases, Zone 1.

Rumach VI

Two cores were examined from Rumach VI. The cores represent the entire RSL history from this site. Four separate zones can be identified in this sequence, Zones 3a and 3b represent the overlap between the two cores. The "Lateglacial core" contains Zones 1 to 3a, which represent Lateglacial to early Holocene sedimentation (from *c.* 12.1 to 9.7 ka cal BP) (Figure 6.6a). The "Holocene core", Zones 3b to 4, record Holocene RSL change (*c.* 9 to 3 ka cal BP) (Figure 6.6b) (Shennan *et al.,* 2000).

The isolation contacts on the new Rumach VI Lateglacial core are placed at 1045 to 1043 cm (between Zones 1 and 2) and at 1000 to 998 cm (Zones 2 and 3) based on diatom stop counts and lithostratigraphic analysis (Appendix II). These contacts correspond to 425 cm and around 340 cm on the published core (Figure 6.6a). No correlations were needed because the same core used for foraminiferal analysis (Lloyd and Evans, 2002) was used for analysis in this thesis.

Lateglacial core

Zone 1 – Lateglacial marine

Zone 1 is characterised by high $\delta^{13}C_{org}$, increasing C/N ratios and TOC values (Figure 6.6a). The $\delta^{13}C_{org}$ values range from –19‰ to –17‰ peaking to –17‰ at 1047 cm. The C/N ratios increase from 9 to 12 and TOC from 0.7 to 2%

(Figure 6.6a). The $\delta^{13}C_{org}$ and C/N ratios plot within and just outside the marine field of Figure 6.7. Based upon the $\delta^{13}C_{org}$ and C/N values from Table 6.2 and Figure 6.7 this zone is interpreted as being dominated by marine aquatics. The data correlates with the biological salinity reconstruction.

Zone 2 – Freshwater loch

The $\delta^{13}C_{org}$, C/N and TOC values show a clear difference from Zone 1. Zone 2 is characterised by low $\delta^{13}C_{org}$, high C/N ratios and TOC values. The $\delta^{13}C_{org}$ values range from –28‰ to –26‰ (Figure 6.6a). The generally high C/N ratios (from 12 to 15) suggest that the majority of the organic material originated from aquatic and increasing amounts come from terrestrial plants towards the top of the zone. This may reflect infilling of the basin and a larger fringe of macrophytes and terrestrial plants. The $\delta^{13}C_{org}$ and C/N plot with the brackish, freshwater aquatic and terrestrial fields defined by the contemporary and published data sets (Figure 6.7). Zone 2 is thought to represent a freshwater environment which the generally high C/N ratios suggest and the organic material originated from aquatic and increasingly from terrestrial plants across the zone. The data correlates with the trend in the biological data (Figure 6.6a).

Zone 3a – Holocene marine

Zone 3a shows a clear difference in $\delta^{13}C_{org}$, C/N ratios and TOC values. The $\delta^{13}C_{org}$ values are approximately 7‰ higher than Zone 2. The $\delta^{13}C_{org}$ range from –22‰ to –19‰, C/N ratios are around 12 and TOC values are around 4% (Figure 6.6a). The organic data plots within the marine field defined by the contemporary and published data set Figure 6.7. Zone 3 forms a well defined field in the C/N vs. $\delta^{13}C_{org}$ biplot (Figure 6.7). The organic material from the Holocene marine zone appears to derive more from aquatic plants in comparison to Zone 1, which received more of its organic material from phytoplankton. This probably reflects the difference in the environmental conditions between the Lateglacial and Holocene. The isotope data corresponds with the biological salinity reconstruction (Figure 6.6a).

Holocene core

The foraminiferal summary (Figure 6.6b) shows a basin with a similar extended Holocene isolation sequence to LNC. At Rumach VI, during the Holocene, RSL fell gradually from 9.0 ka cal BP until the basin became isolated at 3.0 ka cal BP. The isolation process can be divided up into three taxonomic species zones: marine, brackish lagoon and saltmarsh (saltmarsh = brackish environment).

Zone 3b – Holocene marine

Zone 3b in this core overlaps in part with Zone 3a in the Lateglacial core (Figure 6.6a). There is a trend towards high $\delta^{13}C_{org}$ values (from –20‰ to –18‰) that reach a peak between 260 cm to 252 cm. The C/N ratios decrease over Zone 3b from 13 to 10. TOC varies between 4 to 11% (Figure 6.6b). The generally low C/N ratio suggests the sediment is dominated by marine aquatics, however, the presence of phytoplankton cannot be excluded. The data plots within the marine field defined by the contemporary and published results (Figure 6.7). The isotope data and C/N ratios do not correlate with the general trend in the foraminiferal reconstruction. However, TOC mirrors the foraminiferal data suggesting that the aquatic environment is increasing in productivity or becoming less diluted by clastic input.

Zone 4 – Freshwater loch

Zone 4 shows a clear difference in $\delta^{13}C_{org}$, C/N ratios and TOC values from Zone 3b (Figure 6.6b). The carbon isotope values decrease from –21‰ to –29‰, C/N ratio values increase from 11 to 13 across the Zone. TOC increases from 11 to 26% across the boundary zone before peaking at 34% at the top of the core. The organic material from this zone plots within the brackish / freshwater aquatic and terrestrial defined fields in Figure 6.7. The TOC values support the isotope data that a change in aquatic environments has occurred. The increase in TOC can be interpreted as a reduction in minerogenic material diluting the TOC signal. This isotope data clearly shows the transition from a marine / brackish to a freshwater environment. The transition between Zone 3b and Zone 4 corresponds with the end of foraminiferal abundance in the core, which implies that marine inundation had stopped. The diatom reconstruction by Shennan *et al.* (1999) shows the upper section of the basin contained a freshwater loch.

The isotope data clearly distinguishes between the marine and freshwater end-member's phases. However, $\delta^{13}C_{org}$ and C/N ratios did not correspond with the subtle changes in salinity identified by the foraminifera data (Lloyd and Evans, 2002).

Loch nan Corr

The foraminifera summary (Figure 6.8) shows a basin that experienced a gradual reduction in salinity from fully marine conditions at 9.0 ka cal yrs BP before finally becoming isolated from the sea at ~ 0.70 ka cal yrs BP (Lloyd, 2000). The two cores from LNC have been correlated, based upon foraminiferal counts and lithostratigraphic boundaries (Appendix II). The base of the core is devoid of foraminifera; at 713 cm calcareous foraminifera occur and there is an abundance of *Ammonia beccarii*, *Elphidium macellum* and *Cibicides lobatus* which correlates with the basal marine zone in the published data. From 633 cm, the foraminiferal assemblage is dominated by *Haynesina germanica*, which correlate with the brackish lagoon species zone in the original core. By 609 cm, the foraminiferal assemblage is composed of approximately 90% *H.germanica* which corresponds with the saltmarsh species zone on the foraminiferal summary diagram (Lloyd, 2000). The boundary between Zone 2 and Zone 3 is placed at 513 cm, based upon the decline in the *H. germanica,* indicating the decrease in marine influence to the basin. The basin became isolated at 131 cm because no more agglutinated foraminifera were observed in the new core. The core has been divided up into four zones (Figure 6.8).

Zone 1 – Holocene marine

Zone 1 is characterised by high $\delta^{13}C_{org}$ (–22‰ to –20‰) and C/N ratio range from 10 to 14 (Figure 6.8). TOC varies between 4% and 7%. The $\delta^{13}C_{org}$ values plot within the marine and brackish fields and C/N ratios suggest the sedimentary source is from marine aquatics (Figure 6.9). The data from Zone 1 contains the highest $\delta^{13}C_{org}$ values of the core suggesting that this was the most saline part of the core. This interpretation of the isotope data corresponds with the biological salinity trend.

Zone 2 – Brackish basin

Zone 2 is characterised by intermediate $\delta^{13}C_{org}$ and C/N ratios. The $\delta^{13}C_{org}$ value varies between –23‰ to –22‰ and C/N ratio decrease from around 14 to 13. TOC increases steadily from around 5% to 10% from the bottom to the top of Zone 2. The low TOC concentration reflects the influence of a high minerogenic input to the basin. The $\delta^{13}C_{org}$ values plot within the marine and brackish fields (some samples are partially hidden because samples from Zone 3 overlie Zone 2 samples) in Figure 6.9. This suggests that Zone 2 represents a marine to brackish environment which is dominated by aquatics but possibly also received inputs from terrestrial sources. This interpretation is consistent with the foraminiferal summary showing a gradual reduction in basin salinity from Zone 1.

Zone 3 – Brackish basin

Within Zone 3 there is a trend towards decreasing $\delta^{13}C_{org}$ values (from –25‰ to –22‰) to a peak at 177 cm and then an increase to around –22‰ at the top of the zone. The C/N ratios over Zone 3 increase from 14 to 18 (Figure 6.8). TOC values through Zone 3 vary, increasing from 8% to a peak of 13% at 297 cm, values then decline to 1% at 217 cm, but then rise to 7% at the top the zone. The intermediary $\delta^{13}C_{org}$ values suggests Zone 3 represents brackish conditions, in which the values from this zone form a relatively discrete group with only minor overlap with values from Zone 2 and 4 (Figure 6.9). This implies

Zone 3 is less saline compared to Zone 2. This is supported by the foraminiferal data (Figure 6.8). The C/N ratios suggest that Zone 3 received increasing amounts of organic input from terrestrial and aquatic material leading up to the final isolation of the basin. The peak in $\delta^{13}C_{org}$ values, towards the top of Zone 3 (–22‰), is unexpected. This suggests that the basin became slightly more saline before it became isolated. However, the peak in $\delta^{13}C_{org}$ values correlates with the increase in TOC; the increase in TOC levels (from 3% to 8%) indicates that the productivity of the basin increased towards the top of Zone 3.

Zone 4 – Freshwater loch

Zone 4 shows a clear difference in $\delta^{13}C_{org}$ values from Zone 3 by approximately 6‰ over the transition, while C/N ratios increase to 20 at the top of the core (Figure 6.8). The decreasing $\delta^{13}C_{org}$ and high C/N represent freshwater conditions. Samples from Zone 4 overlap across all data fields in the C/N vs. $\delta^{13}C_{org}$ plot (Figure 6.9). The overlap across the fields shows the transition from a brackish/marine environment to a freshwater loch. The relatively high C/N ratios suggest that the source of organic material is increasingly derived from terrestrial sources across the zone

Overall, the isotope data from LNC correlates reasonably well with the trend in the foraminiferal salinity reconstruction.

Lateglacial sediment sequences from Arisaig

Four Lateglacial basins (Upper Allt Dail An Dubh-Asaid, Torr a'Bheithe, Loch Torr a' Bheithe and Loch a' Mhuilinn, Figure 3.2) were examined from Arisaig to establish if the palaeoenvironment of the Lateglacial is recorded in the bulk $\delta^{13}C_{org}$ values within the sediment.

Upper Allt Dail An Dubh-Asaid

Upper Allt Dail An Dubh-Asaid (UADD), with a sill altitude of + 61.88 m OD, is the highest of the Arisaig basins and higher than any previously studied basin with a Lateglacial marine zone. UADD is believed to lie above the Lateglacial marine limit of the area because no marine diatoms have been found in this basin (Shennan *pers. comm.*). This basin was sampled to provide a range of end-member values for Lateglacial freshwater sediment in Arisaig. UADD has C/N ratios that range between 8.7 to 9.9 and $\delta^{13}C_{org}$ values from –23.7‰ to –20.2‰ (Figure 6.10). These values plot within the marine and brackish zones identified in Figure 6.11. This indicates that Lateglacial freshwater bulk $\delta^{13}C_{org}$ sediment from UADD is isotopically indistinguishable from Holocene and contemporary marine/brackish sediment.

Torr a' Bheithe

Based on the biological reconstruction, Torr a' Bheithe (TB) became isolated at 15429 – 14595 (15033) cal yrs BP due to Lateglacial RSL fall (Shennan *et al.*, 2000). The isolation contact on the published diatom summary diagram at 780 cm equates to 777 cm on the new core (Figure 6.12). The cores were matched up based on lithostratigraphic interpretation and two diatom spot counts (Appendix II). TB can be subdivided into 4 main zones based upon the four main lithostratigraphic zones.

Zone 1 – Lateglacial marine

The low organic content (<0.3%) prevented the majority of the samples being analysed for $\delta^{13}C_{org}$ from Zone 1. However, two samples which were successfully analysed from Zone 1 have high $\delta^{13}C_{org}$ values (–17‰) and low C/N ratios (6.7-7.8) (Figure 6.12). The data plots within the marine field defined by the contemporary data set (Figure 6.13). The generally low C/N ratios (7 to 8) and high $\delta^{13}C_{org}$ values suggest the majority of the organic material most likely originated from marine plankton and some aquatic plants based on the values in Table 6.2. The interpretation of the isotope data from Zone 1 corresponds with the biological reconstruction (Shennan *et al.*, 2000).

Zone 2 – Freshwater loch

Zone 2 shows a clear difference in TOC values from Zone 1 which range from 0.5% to 10.7% at the top of the zone. The C/N ratios increase over the zone from 10 to 13 (Figure 6.12). This suggests a change in the organic source such as an increase in the amount of terrestrial or aquatic material compared to plankton. The $\delta^{13}C_{org}$ range around –20‰ to –18‰ and plot inside the marine field defined by the contemporary data set (Figure 6.13). The interpretation of the isotope data in Zone 2, does not correspond with the biological reconstruction which suggests freshwater conditions (Shennan *et al.,* 2000). However, the TOC data is mirroring the trend in the salinity reconstruction. This is interpreted as reflecting the reduction in clastic material arising with the end of inundation to the basin.

Zone 3 –Freshwater loch

Zone 3 is thought to represent freshwater sediment deposited during the Younger Dryas chronozone, because Zone 3 has a high clastic content and is surrounded by organic limnus deposited during the Lateglacial (indicated by isolation contact date). Zone 3 is characterised by a shift in the values of all three proxies. The $\delta^{13}C_{org}$ values decrease to –20.4‰ at 745 cm. This correlates with a peak in C/N of 15 and a decline in TOC from 11% to 7% (Figure 6.12). The $\delta^{13}C_{org}$ and the C/N ratios plot within and just beyond the marine field defined in Figure 6.13. Combined with the data from Table 6.2, the isotope data suggests that the organic matter originated from marine aquatic sources. However, the peak in C/N ratio (15) indicates that there was an increase in the amount of terrestrial organic matter to the basin. Again, the interpretation of the isotope data from Zone 3 does not correspond with biological reconstruction for this zone (Figure 6.12). The TOC data suggest that there is a decline in the productivity of the aquatic environment.

Zone 4 – Freshwater loch

Only two samples have been analysed from Zone 4. Zone 4 shows a clear difference in C/N ratios (from 14 to 11) from Zone 3, also the $\delta^{13}C_{org}$ values are slightly lower compared to Zone 3. The top of the core records a $\delta^{13}C_{org}$ value of –21.4‰ and the TOC is around 10% (Figure 6.12). The samples from this zone plot within the marine field of Figure 6.13, which implies that the organic material originated from marine aquatic sources. Again the interpretation of the isotope data does not correspond with the biological reconstruction for this zone.

Loch Torr a' Bheithe

Based on diatom and foraminiferal analysis, LTB became isolated from the sea at 15251 - 14435 (14843) cal yrs BP (Shennan *et al.,* 2000). The isolation contact of the published core is 558 cm; this corresponds to 553 cm on the new core, based upon lithostratigraphic analysis and diatom spot counts (Figure 6.14). The sediment sample at 550 cm is dominated by oligohalobous forms, such as *Opephora martyi* and *Fragilaria constueus* (Appendix II). Unfortunately, all samples below 550 cm are devoid of diatoms, but, the lithostratigraphic analysis suggests that the isolation contact is at 553 cm. Based upon the lithostratigraphy and diatom summary (Shennan *et al.,* 2000), LTB can be divided into four zones. However, the original core analysed for the biological reconstruction was much shorter (only 16 cm long), compared to the new core, and it appears that Zones 3 to Zone 4 are missing from the published core, based on the lithology (Figure 6.14)

Zone 1– Lateglacial marine

The carbon content of the samples, from Zone 1, are very low (around 0.7%) and only three samples could be analysed for $\delta^{13}C_{org}$. Zone 1 is characterised by a broad spread of values; $\delta^{13}C_{org}$ range from –23‰ to –18.5‰ and C/N ratios range between 9 and 7 (Figure 6.14). The $\delta^{13}C_{org}$ values plot within the marine and brackish fields (Figure 6.15). The generally low C/N ratios imply that the majority of the organic material originated from aquatic plants and phytoplankton (Figure 6.16 and Table 6.2). This interpretation corresponds with the biological reconstruction (Figure 6.16).

Zone 2 – Freshwater loch

Zone 2 shows a clear difference in TOC values from Zone 1, from 0.7 to 10%, to a peak at around 520 cm of 12% and then decrease to around 7% at the top of the zone. The carbon isotope ratios are similar to the values recorded in Zone 1. At the base of the zone, $\delta^{13}C_{org}$ values are –20.1‰ and peak to –16.9‰ at 520 cm. This correlates with a peak in both C/N ratios and TOC, recording values of 14.3% and 12.2% respectively. The $\delta^{13}C_{org}$ values become progressively lower towards the top of the zone. At the top of Zone 2, $\delta^{13}C_{org}$ records a value of –19.1‰. A similar trend is seen in both C/N ratio and TOC values. C/N ratios fall to 12 and TOC declines to 7% (Figure 6.14). The falling TOC values probably indicate a reduction in productivity although sediment dilution could also cause TOC to decline. The $\delta^{13}C_{org}$ values plot within the marine field (Figure 6.15), which implies that the organic matter originated from marine aquatic plants and phytoplankton (Figure 6.15 and Table 6.2). This interpretation does not correspond with the biological reconstruction.

Zone 3 – Freshwater loch

Zone 3 is thought to represent freshwater Younger Dryas sediment because of the high minerogenic content of this zone which is surrounded by Lateglacial organic limnic material. Zone 3 is characterised by a peak in both $\delta^{13}C_{org}$ and TOC values (Figure 6.14). The $\delta^{13}C_{org}$ sample at 505 cm increases to –16.9‰ and corresponds with a low TOC value of 3.5%. This peak correlates with a decline in TOC values from 6.9% to 3.5% suggesting a decline in lake productivity or an increase in sediment dilution caused by higher levels of inwashing of minerogenic material. The C/N ratios remain relatively unchanged from the top of Zone 2 through Zone 3. The $\delta^{13}C_{org}$ values plot within the marine field of Figure 6.15. The high $\delta^{13}C_{org}$ and the low TOC values are interpreted as reflecting the environmental influences associated with the Younger Dryas. Other European lacustrine records attribute high $\delta^{13}C_{org}$ and low TOC values during the climate deterioration of the Younger Dryas chronozone (Hammarlund, 1993; Turney *et al.,* 1999; Nuñez *et al.,* 2001).

Zone 4 – Freshwater loch

Only one sample characterises Zone 4. In this, the $\delta^{13}C_{org}$ value is lower compared to Zone 3 and has a value of –21.0‰, TOC increases to 7.4% and the C/N ratio is 9.6 (Figure 6.14). Values from Zone 4 plot within the marine zone defined in Figure 6.15. The C/N ratios are typical of aquatic organic matter.

The diatom reconstruction suggests a change from brackish to freshwater environment across the isolation contact due to RSL fall. The isotope data does not support this interpretation.

Loch a' Mhuilinn

The results from the new core, collected from LAM, are presented in Figure 6.16, alongside a summary of the diatom flora from the nearby core investigated by Shennan *et al.* (2000). The isolation contact of the original core is at 647cm, this is equivalent to 750 cm on the new core, based on the lithostratigraphic interpretation and two diatom spot counts (Appendix II). Based on the diatom flora (Shennan *et al.,* 2000) and lithostratigraphy, LAM can be divided up into two zones. The diatom summary shows that Zone 1 experienced marine/brackish conditions which changed to a freshwater environment in Zone 2, due to Lateglacial RSL. Fall (Figure 6.16).

Zone 1 – Lateglacial marine

Zone 1 is characterised by high $\delta^{13}C_{org}$ values (–21‰ to –19.6‰) and low C/N ratios ranging from 6.3 to 8.5. The TOC values are extremely low and remain stable around 0.2% (Figure 6.16). The majority of the $\delta^{13}C_{org}$ values plot within the marine field identified in Figure 6.17. The low C/N ratios suggest that organic matter originated from a mixture of marine aquatics and phytoplankton.

Zone 2 – Freshwater loch

Zone 2 is characterised by high $\delta^{13}C_{org}$ and low C/N ratios, except for a single excursion in the $\delta^{13}C_{org}$ values at 741 cm, where the sample records a significantly lower value of –23.5‰, relative to the rest of Zone 2. This is not matched by a fluctuation in either the C/N or TOC values. The C/N values (around 9) indicate that the organic mater was derived mainly from aquatic plants and phytoplankton (Table 6.2). The $\delta^{13}C_{org}$ values plot within the marine field identified in Figure 6.17. The isotopic data do not follow the trend in the biological data. However, the TOC profile shows an abrupt increase in values at the transition, from Zone 1 to 2, from 0.2% to 9% correlating with the trend in the biological data (Figure 6.16). TOC maybe reflects the reduction in minerogenic dilution associated with a change in aquatic environment.

The diatoms show a change from marine/brackish to freshwater conditions due to falling RSL. The trend in the $\delta^{13}C_{org}$ values and C/N ratios remain stable down core and do not correlate with the biological profile. The TOC profile shows the most variation, dramatically increasing at the transition from Zone 1 to 2 corresponding with the biological salinity reconstruction. TOC is assumed to be reflecting a reduction in minerogenic input associated with the removal of marine conditions.

6. 4 Discussion

6.4.1 Holocene basins

The results show that variations in the $\delta^{13}C_{org}$ values and C/N ratios from ULNE, MLNE, Rumach VI and LNC correlate with the general trends in the biological salinity reconstructions. The results from these four sites show salinity is the dominant control on the $\delta^{13}C_{org}$ and C/N signal. Diagenetic influences do not appear to mask the $\delta^{13}C_{org}$ difference between freshwater and marine end-members values in the sediment cores. Also, C/N clearly distinguishes between aquatic and terrestrial plants. By using the two proxies in tandem, subtle changes in salinity can be identified and even the brackish environment can be characterised; this can be seen in the data from ULNE. The results from LNC show that $\delta^{13}C_{org}$ and C/N ratios can be used as palaeosalinity indicators in a field area other than Arisaig (the main field site). However, the $\delta^{13}C_{org}$ and C/N ratios from the Holocene section of Rumach VI (Zone 3) and $\delta^{13}C_{org}$ values just before LNC becomes isolated (Zone 3, 169 cm to 137 cm) are more difficult to interpret. The isotope data clearly distinguishes between the marine and freshwater end-member's phases. However, $\delta^{13}C_{org}$ and C/N ratios did not correlate with the subtle changes in salinity, identified by the foraminifera data (Lloyd and Evans, 2002). The isotope data could be reflecting something specific about this site. A likely possibility is that, the gradual reduction in marine inundation led to an increase in aquatic productivity, indicated by the gradually increasing TOC values through Zone 2, from around 5% to 10%. The increase in productivity would have caused the TDIC to become enriched in the heavier isotope ^{13}C due to preferential utilisation of ^{12}C. Aquatic plants and phytoplankton, utilising the enriched TDIC pool, will have higher $\delta^{13}C_{org}$ values (Herczeg and Fairbanks, 1987). The similar process could also explain the shift to higher $\delta^{13}C_{org}$ values before the isolation contact of LNC, as the rise in $\delta^{13}C_{org}$ values correspond with a rapid increase in TOC values. This implies that $\delta^{13}C_{org}$ can be used to reconstruct basin dynamics (e.g. changes in aquatic productivity) during an isolation process. The different results between LNC and the Holocene section of Rumach VI show that more research needs to be undertaken to understand how slowly isolated sequences preserve biological and geochemical indicators of salinity, as well as understanding the complex changes in the aquatic environment associated with isolation events.

The data also suggest that, once within the marine realm it is difficult to differentiate changes in RSL that may be recorded in the biological flora and fauna. This idea can be tested by comparing Holocene marine $\delta^{13}C_{org}$ values from ULNE, MLNE and Rumach VI because they form a staircase of basins which record a similar RSL history (Figure 6.18). At any specific time RSL in Rumach VI>MLNE>ULNE, therefore the $\delta^{13}C_{org}$ values should be higher (i.e. "more marine") in Rumach VI than MNLE or ULNE because Rumach VI is lower down the staircase sequence and should receive greater marine input compared to ULNE. Also the water depth of Rumach VI will be deeper and remain saline for longer than ULNE for a given marine interval (Figure 6.18). For example Rumach VI has a sill altitude 2 m lower than ULNE, so during a marine phase Rumach VI will have greater marine inundation, with a marine water depth 2 m greater than ULNE and remain saline for approximately 1800 years longer than Rumach VI (difference between dates of Holocene isolation contacts). During the Holocene marine phase, the $\delta^{13}C_{org}$ values for all three basins are similar. The majority of the $\delta^{13}C_{org}$ values for all three basins overlap with one another, $\delta^{13}C_{org}$ values range between –20‰ and –17‰ (Figure 6.19). Overall, the data does not show the expected trend, this is supported by data from Zones 4 and 6 ULNE. Zone 4 records higher $\delta^{13}C_{org}$ values and Zone 6, whereas the diatom flora suggests Zone 6 had a greater marine input than Zone 4 (Figure 6.2, 6.3). Therefore once in the marine phase it is hard to differentiate changes in sea-level that may be recorded in the diatom flora. The data from these three basins highlights the limits of the methodology. The data shows that marine aquatics have a range of $\delta^{13}C_{org}$ values independent of water depth and possible minor changes in salinity.

6.4.2 Palaeoclimatic influences on $\delta^{13}C_{org}$ signature from isolation basins

The Lateglacial Interstadial (ca. 14.0 to 12.6 ka cal yr BP) across the North Atlantic region was characterised by a number of extreme climate events (Walker *et al.*, 2003) and global atmospheric CO_2 levels were lower (e.g. 251 ± 31 ppmv during the Younger Dryas compared to 280 ppmv in the Holocene;

Anklin *et al.*, 1997)). For example the Younger Dryas Stadial (Greenland Stadial 1) ca. 12.6 to 11.4 ka cal BP, mean July temperatures were around 10-11°C a drop of around 10°C from a maximum at the beginning of the Interstadial (Walker *et al.*, 2003). There were also a number of smaller short-term climate deteriorations prior to the Younger Dryas event, for example at 13.1 ka cal BP (Walker *et al.*, 2003). These palaeoclimatic shifts and variations in CO_2 levels could have had a significant impact on $\delta^{13}C_{org}$ values from Lateglacial isolation basin sediments. The results from UADD, LAM, LB and LTB, show that during the Lateglacial and during the Younger Dryas chronozone, the relationship found throughout the Holocene between $\delta^{13}C_{org}$, C/N and salinity does not exist. The $\delta^{13}C_{org}$ values from UADD (the freshwater Lateglacial end-member basin) plot within the marine field of Figure 6.4. The data show that Lateglacial freshwater sediment is indistinguishable from Lateglacial marine or brackish samples. The results, from the freshwater sections of LAM, TB and LTB substantiate this finding. At all four Lateglacial basins the freshwater material has $\delta^{13}C_{org}$ values consistent with marine or brackish material, identified by the contemporary and published data set (Figure 6.11, 6.13, 6.15, 6.17). The C/N ratios tend to be slightly higher in Lateglacial freshwater sediment compared to marine Lateglacial sediments, but it is still difficult to distinguish between Lateglacial marine and freshwater environments based on C/N ratios because all the values are similar to aquatic plants. Hence, without a clear signal from $\delta^{13}C_{org}$, the marine and freshwater Lateglacial environments cannot be distinguished.

This implies that an alternative palaeoenvironmental variable had the largest influence on $\delta^{13}C_{org}$. The isotopically high $\delta^{13}C_{org}$ values, recorded from the freshwater section of UADD, LAM, LTB and TB, are consistent with $\delta^{13}C_{org}$ from other freshwater Lateglacial deposits in Scotland. For example, Turney (1999) examined five Lateglacial-Holocene transition lake sequences (ca. 14-9 ka ^{14}C BP) across Britain and found that $\delta^{13}C_{org}$ records from England, Wales and southern Scotland recorded a shift to isotopically lighter values ca. 13.80 –

13.65 ka cal BP. Turney interpreted this shift as a response to water stress during colder climatic conditions and lower CO_2 levels. However, a site in the far north of Scotland, Borrobol, did not record a shift in $\delta^{13}C_{org}$ values until after the Younger Dryas event, even though summer temperatures during the Lateglacial Interstadial are estimated to have been around 13 – 15°C (Lowe *et al.*, 1995). Turney (1999) suggested the results from Borrobol reflected poor soil and vegetation development in the catchment causing TDIC of lake waters to remain isotopically high due to the lack of isotopically low carbon from soil and terrestrial plant matter (–27‰). Arisaig, situated on the exposed northwest coast of Scotland, could have experienced similar catchment responses to the Borrobol site. This is indicated by the low TOC content of the sediments and the dominance of aquatic plants in the basins at all four sites (TOC around 1-10%, C/N between 8 to 12). Mature terrestrial vegetation development might have been prevented because all four sites are situated above the main valley floor in Arisaig and therefore relatively exposed; Loch a' Muilinn is also surrounded by steep slopes which would have restricted soil and vegetation development under repeated climatic fluctuations. Even if the aquatic vegetation responded to Lateglacial Interstadial warming, indicated by increases in the TOC content of the sediments (e.g. UADD, TOC increased from 1 to 8%), the TDIC pool would have quickly become enriched in the heavier isotope ^{13}C due to preferential utilisation of ^{12}C (Herczeg and Fairbanks, 1987). Aquatic $\delta^{13}C_{org}$ values would have remained high throughout the Lateglacial Interstadial if the basins were receiving little carbon input from soil and terrestrial vegetation matter. In addition, the basins would have been influenced to a greater extent by atmospheric CO_2. The CO_2 concentration, during the Lateglacial Interstadial, is thought to have been lower than present day; also the $\delta^{13}C$ values was around –6.8‰ compared to the present day value of –7.8‰ (Leuenberger *et al.*, 1992). At a temperature of 10°C fractionation between $CO_{2(g)}$ and $HCO^{-}_{3(aq)}$ is +9.6‰ (Mook *et al.*, 1974). This would lead to TDIC with a value of +2.8‰ which would cause aquatic plants to record high $\delta^{13}C_{org}$ values.

The high $\delta^{13}C_{org}$ values from the Younger Dryas sediment in TB and LTB are likely to be a result of poor soil and vegetation cover caused by the rapid cooling event. However, the results from TB and LTB differ. The isotope data from TB show a peak towards lower values just before the onset of the Younger Dryas, while LTB showed the reverse trend. Possibly the lower $\delta^{13}C_{org}$ and high C/N ratios from TB represent the erosion of the catchment and the in wash of terrestrial vegetation to the basins associated with the deterioration in palaeoclimate. A number of Younger Dryas sequences record a similar trend in the $\delta^{13}C_{org}$ values in the middle of the Younger Dryas event, for example, Borrobol, North Scotland, investigated by Turney (1999). Overall, the combination of poor, mature vegetation cover and lower atmospheric CO_2 levels is the likely cause of high $\delta^{13}C_{org}$ values from UADD, TB, LTB and LAM throughout the Lateglacial Interstadial on these exposed basins which masked the influence of palaeosalinity.

Even though $\delta^{13}C_{org}$ values appear to be problematic in Lateglacial isolation basin sediments, the TOC data show a consistent offset between marine and freshwater sediment which mirrors the general biological salinity reconstruction. In all three Lateglacial isolation basins there is a sharp increase in TOC values from <0.5% to around 8-10%. The relationship between TOC and the biological salinity reconstruction is due to the increase in clastic sediment influx during marine conditions and greater *in situ* productivity during freshwater conditions. However, productivity may have increased due to the change in water temperature between marine and freshwater environments.

Younger Dryas

ULNE, MLNE and Rumach VI do not show a Younger Dryas signal in the $\delta^{13}C_{org}$. This probably reflects site specific characteristics. ULNE, MLNE and Rumach VI are all well sheltered sites situated in the main valley which is surrounded by large catchments relative to the other Lateglacial sites in the area. These three sheltered sites may have retained a more developed vegetation catchment compared to the more exposed sites such as TB or LTB, this is indicated by ULNE, MLNE and Rumach VI high TOC contents (e.g. ULNE around 15%) after the basins have been isolated for the first time. Another possibility is that the sampling resolution was insufficient to detect such a short-lived palaeoenvironmental occurrence. The Younger Dryas event was only recorded by 8 cm of inorganic material in TB and 3 cm in LTB. If the Younger Dryas was expressed by <10 cm of sediment, the sampling resolution of 4 to 8 cm in the freshwater sections of the cores of ULNE, MLNE and Rumach VI, might have resulted in the event being unsampled, especially due to the lack of lithological evidence.

Also, not many Younger Dryas lake sediments in the UK record $\delta^{13}C_{org}$ values equivalent to marine or brackish environments which would help to identify the event. For example, at the five Lateglacial sites examined by Turney (1999), only one site Borrobol, Northern Scotland, has high $\delta^{13}C_{org}$ values (–24‰ to –20‰) similar to marine and brackish sediments during the Younger Dryas. At the other four sites the $\delta^{13}C_{org}$ values are similar to contemporary and Holocene freshwater aquatic and terrestrial matter; Gransmoor, northeast England has a range of $\delta^{13}C_{org}$ values between –28‰ to –26‰, Llanilid, south Wales, Whitrig Bog, southern Scotland –28‰ to –25‰ and Tynaspirit West, western Scotland –29‰ to –25‰. It can been seen that Turneys' four UK lake Younger Drays sediments increased slightly (around 4‰) in $\delta^{13}C_{org}$ values over the duration of the climate event, however, the $\delta^{13}C_{org}$ values fall within the range of freshwater contemporary and Holocene sediments (Table 6.2). Turney explains the difference between the Borrobol site (the site which has higher than 'normal' $\delta^{13}C_{org}$ freshwater values) and the four sites that have a Younger Dryas signature similar to 'normal' freshwater values is due to the difference in catchment vegetation cover and degree of soil stability. The results from Tynaspirit West are surprising, considering the basin lies only 2.5 km beyond the Younger Dryas limits. This shows that Younger Dryas lake sediment, very near the limits of the Younger Dryas ice sheet, do not record values dissimilar to Holocene lake sediments. This may also explain why ULNE, MLNE and Rumach VI do not show evidence of a Younger Dryas event. Overall, it is difficult to identify the reason for the lack of Younger Dryas signal in ULNE, MLNE and Rumach VI. It is likely that a combination of all the above factors could explain the difference between ULNE, MLNE, Rumach VI and the four higher Lateglacial basins, UADD, LTB, TB and LAM.

In summary, the isotope data from Lateglacial archives, older than 12.4 ka cal BP, are adversely affected by palaeoclimatic influences and therefore the $\delta^{13}C_{org}$ and C/N ratios cannot be used to distinguish between Lateglacial marine and freshwater conditions. However, the TOC data show promise in helping to support the biological salinity reconstructions from Lateglacial isolation basin sediments. However, TOC is not an alternative indicator of salinity, because minerogenic sediment can be deposited during periods of deglaciation or cooler climates. A number of basins (e.g. UADD) above the marine limit in Arisaig contain a clastic to organic transition (like an isolation contact) but experienced no marine influence. The clastic material was deposited during deglacialation of the area.

6.5 Conclusion

1. Analysis of $\delta^{13}C_{org}$ values of present day plant material, within and around contemporary isolation basins, reveal a large difference (>5‰) between marine and freshwater organic material. Bulk sediment from marine and freshwater environments concur with the contemporary data, providing for the first time clear end-member ranges for organic material isotopic composition from isolation basins in NW Scotland.
2. Variations in the $\delta^{13}C_{org}$ values and C/N ratios from Upper Loch nan Eala, Main Loch nan Eala, Rumach VI and Loch nan Corr, in general, follow the biologically based palaeosalinity reconstructions. Therefore,

changes in marine inundation controlling basin salinity appear to be a significant factor controlling the source of organic material producing the distinctive $\delta^{13}C_{org}$ and C/N signatures.

3. Caution is required when applying $\delta^{13}C_{org}$ and C/N ratios to extended isolation sequences. The method will successfully identify the isolation contact, however, variations in the $\delta^{13}C_{org}$ values and C/N ratio during the brackish phases may be influenced to a greater extent by basin productivity. By using $\delta^{13}C_{org}$, C/N ratios and TOC values in combination, the complex change in the aquatic environment during an isolation event can be reconstructed for the first time.
4. Once in the marine phase the absolute values of $\delta^{13}C_{org}$ cannot differentiate between 'more' or 'less' marine environments.
5. Variations in the $\delta^{13}C_{org}$ values and C/N ratios from Lateglacial sediments, older than 12.4 ka cal BP, cannot be used to distinguish between marine and freshwater phases. Other environmental variables, such as temperature and atmospheric CO_2, are dominant during this period. However, the use of TOC as a proxy can be used to support biological RSL reconstruction of Lateglacial age.
6. The combination of $\delta^{13}C_{org}$, C/N ratios and TOC values provides an alternative method for palaeosalinity reconstruction for sediment of Holocene age. This combination of proxies provides a suitable method of palaeosalinity reconstruction where sediments are devoid of microfossils.

Chapter 7

The application of oxygen and carbon isotope ratios from foraminifera as salinity proxies for isolation basin sediments

7.1 Introduction

This chapter presents the results of oxygen and carbon isotope ratios ($\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$), from the benthic calcareous foraminiferal species *Haynesina germanica,* applied to the fossil isolation basin Loch nan Corr (LNC), Kintail (location map Figure 3.1, 3.21). The species *H. germanica* is an infaunal species and tolerant of a wide range of salinities (Murray, 1979). Thus it is found in abundant concentrations in fossil isolation basin sediments (Lloyd, 2000). Previous research has shown that *H. germanica* is a suitable species for stable isotope analysis for palaeosalinity reconstructions within fossil isolation basin sediments (Lloyd and Evans, 2002). The $\delta^{18}O_{foram}$ signal is a reflection of $\delta^{18}O_{w}$ (which is related to salinity), water temperature (–0.24‰/°C) and species vital effects at the time of carbonate secretion. Isolation basin waters from Northwest Scotland are a mixture of meteoric and ocean waters. Meteoric waters are isotopically lower (annual mean precipitation is ~ –6.5‰ SMOW Darling *et al.*, 2004) than average ocean water (~ 0‰ SMOW Hoefs, 1987). The $\delta^{13}C_{foram}$ signal is a reflection of changes in the TDIC composition between fresh and marine water and to a lesser extent, temperature effects. Freshwater generally has lower $\delta^{13}C_{TDIC}$ (typical range from British Isles rivers and streams ~ –12‰ to –5‰ PDB, Andrews *et al.*, 1993) relative to marine water due to the influences of isotopically low terrestrial carbon. Average ocean surface water has a $\delta^{13}C$ of ~+2‰ (Beveridge and Shackleton, 1994). Hence, the greater amount of freshwater flowing into the isolation basin, the lower $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ values will become, since the effect due to temperature changes is relatively small (see section 2.6.2 for further details of isotopic systematics). This will be done by examining the relationship between the isotopic concentration of basin waters ($\delta^{18}O_w$, $\delta^{13}C_{TDIC}$) and foraminifera ($\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$) from the three contemporary isolation basins (Rumach Tidal Pond (RTP), Craiglin Lagoon and freshwaters of Loch nan Corr (LNC)) (Figure 3.2, 3.21, 2.24) to salinity and temperature between seasons. The contemporary observations will be used to understand the down-core measurement on the species *H.germanica* from LNC. The results from this study will be compared with the faunal palaeosalinity reconstruction of LNC (Lloyd, 2000).

$\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ have previously been analysed from LNC (Lloyd and Evans, 2002), although the paleosalinity reconstruction was based upon limited contemporary data. Lloyd and Evans (2002) speculated that changes in the source of organic matter might be the controlling variable for $\delta^{13}C_{foram}$ through the core, but they did not test this hypothesis. This study attempts to expand upon this earlier study by collecting detailed water chemistry data i.e. salinity, temperature, pH, dissolved oxygen concentration, $\delta^{13}C_{org}$ for surface sediment and $\delta^{18}O_w$ and $\delta^{13}C_{TDIC}$ to establish their relationship to $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$.

In addition, the new core extracted from LNC has also been analysed for $\delta^{13}C_{org}$ and C/N ratios. Consequently, the influence of changes in organic carbon sources on $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ can be more rigorously established.

7.2 Results

7.2.1 Contemporary data

Due to the lack of contemporary foraminifera at RTP and Craiglin Lagoon, the relationship between salinity and temperature cannot be examined. Although there is limited contemporary water data, it does provide some useful insights into the sources of water within isolation basins and how actual foraminifera fractionation occurs during the marine and brackish phases in which foraminifera live.

Figure 7.1a and 7.1b shows a plots of $\delta^{18}O_w$ and $\delta^{13}C_{TDIC}$ vs. salinity from samples taken within each basin. The $\delta^{18}O_w$ data (Figure 7.1a) show a very strong relationship with salinity between the three basins ($R^2 = 0.95$). The most negative values correlate with the least saline conditions. RTP contains the highest values, with minor overlap with Craiglin Lagoon and LNC records the lowest $\delta^{18}O_w$ values. The freshwater values are similar at all three sites and closely reflect $\delta^{18}O$ for mean annual precipitation values for NW Scotland (–7‰ to –5‰, Darling *et al.* (2004)). The $\delta^{13}C_{TDIC}$ vs. salinity biplot (Figure 7.1b) does not show the same relationship with salinity ($R^2 = 0.06$). The freshwater samples from Craiglin Lagoon and LNC are within the typical range for groundwater in the UK $\delta^{13}C_w$ (Darling *et al.*, 2003), except for RTP which suggests input from lower carbon reflecting more terrestrial sources. Figure 7.2a and 7.2b show a biplot of $\delta^{18}O_w$ and $\delta^{13}C_{TDIC}$ vs. temperature from samples taken within each basin. Both diagrams show there is no correlation with temperature ($R^2 = 0.04$ and 0.02). Overall, there is a good relationship between $\delta^{18}O_w$ and salinity in the three basins and temperature does not play a role because the environmental influence of salinity is significantly greater than temperature. The $\delta^{13}C_{TDIC}$ signal is more complicated and is not controlled by salinity. However, the individual basins show different relationship between $\delta^{18}O$ / $\delta^{13}C$ and salinity, especially from the brackish phase (Craiglin Lagoon). These will briefly be examined in RTP and Craiglin Lagoon; LNC is not examined because there are insufficient samples from each season to determine reliable relationships.

Rumach Tidal Pond

The $\delta^{18}O_w$ vs. salinity biplot (Figure 7.3a) shows a very strong relationship between salinity and $\delta^{18}O_w$ ($R^2 = 0.97$). The basin waters and the waters taken from seaward of basins sill are higher (0.2 to –1.7‰) than the samples from the two streams (–5.8‰ to –4.9‰).

Figure 7.3b shows the biplot of $\delta^{18}O_w$ vs. temperature. The data shows that water temperatures were lower in May (around 12-13°C) compared to August (around 14 -15°C). However, $\delta^{18}O_w$ values show no relationship to temperature (Figure 7.3b). For example stream waters have similar water temperature as basin and waters seaward of the sill but have different $\delta^{18}O_w$ (–5.8‰ to –4.9‰ compared to 0.2‰ to –1.7‰ respectively).

Figure 7.4a is a biplot of $\delta^{13}C_{TDIC}$ vs. salinity and shows there is a significant relationship ($R^2 = 0.78$). The $\delta^{13}C_{TDIC}$ values from water samples collected within the basin and seaward of the sill of RTP range from –6.7‰ to –8.2‰. These values for marine $\delta^{13}C_{TDIC}$ shows the influences of terrestrial low carbon, typically ocean $\delta^{13}C_{TDIC}$ is ~ 0‰ (Figure 2.1). There is only one value for the freshwater input into RTP (because the dissolved inorganic carbon content in the freshwater streams is extremely low), which is considerably lower (–15.8‰) than samples taken from within the basin and seaward of the sill. This is probably a function of the stream water mixing with the marine water. This value clearly shows the influence of low terrestrial carbon. The data shows that the basin TDIC is not influenced by freshwater TDIC, except during very low water in the basin created during a low and spring tide event. For example, at the low tide, spring tide, a sample taken near the location of stream 2 (Station 5) records a $\delta^{13}C_{TDIC}$ value of –10.2‰ (salinity 21psu), this low value reflects the possible influence of freshwater carbon into the basin, however, this is the only sample from RTP which records such a low value. Figure 7.4b is a biplot showing $\delta^{13}C_{TDIC}$ vs. temperature. There is no relationship found (R^2 = 0.01), although temperatures in May were lower than August, the $\delta^{13}C_{TDIC}$ values for samples taken within the basin and seaward of the sill between May and August were very similar. Overall, the $\delta^{13}C_w$ data shows a relationship with salinity (but weaker than $\delta^{18}O_w$) and no relationship with temperature.

Craiglin Lagoon

As described in Chapter 3 Craiglin lagoon is stratified, with a halocline at its deepest sections (i.e. between Stations 1 to 3 - it is unknown if it is permanent) (Figure 3.23). The halocline is less pronounced in October compared to August. Surface water during August is around 15psu while the bottom waters range between 27-30psu. In October, surface waters become more saline with values of around 25psu, while bottom water salinity remained constant ranging between 27-30psu (Figure 7.5a). There is a relationship between $\delta^{18}O_w$ and salinity (R^2 = 0.63) (Figure 7.5a) and also with temperature (R^2 = 0.58) (Figure 7.5b). All the $\delta^{18}O_w$ values from within the basin and seaward of the sill are within error of standard North Atlantic water (Hoefs, 1997). The $\delta^{18}O_w$ value for stream input is –6.4‰, which is significantly lower than the samples from the basin and seaward of the sill. Overall, $\delta^{18}O_w$ signal is influenced by both salinity and temperature; the $\delta^{18}O_w$ relationship with salinity is dominant as the relationship is stronger compared to temperature. The relationship with temperature occurs by chance due to the difference in water temperature between October and August.

The $\delta^{13}C_{TDIC}$ data from Craiglin Lagoon are markedly different to the data from RTP, as $\delta^{13}C_{TDIC}$ appears not to reflect the influence of salinity or temperature upon its signal (Figure 7.6a, 7.6b). Values range from –10.0‰ to –5.2‰, reflecting groundwater values. Unfortunately, no geochemical data could be analysed (due to insufficient dissolved carbonate for analysis) from the stream water to get a freshwater end member value from this location. It is likely that the $\delta^{13}C_{TDIC}$ value would be similar to RTP freshwater streams because the vegetation of the catchments is similar. Figure 7.6a,b shows a biplot of $\delta^{13}C_{TDIC}$ vs. salinity and temperature, again no relationship is found (R^2 = 0.12 and 0.16 respectively). The difference between the sites is not readily understood and the stratified basin at Craiglin Lagoon may complicate the relationship between different sources of carbon.

Overall, the $\delta^{18}O_w$ from all three contemporary basins shows a clear relationship with salinity. This suggests that if foraminifera from LNC secrete calcite in isotopic equilibrium, a pattern related to salinity should emerge even without consideration of any fractionation effects due to temperature. However, this relationship might not hold true in the brackish phases. The contemporary data set for $\delta^{13}C_{TDIC}$ shows there is no relationship with salinity or temperature. However, the data from RTP suggest that in the marine phases the $\delta^{13}C_{TDIC}$ signal could be related to salinity but is probably complicated by multiple sources of carbon. Overall, the $\delta^{13}C_{TDIC}$ data implies that $\delta^{13}C_{foram}$ will not show a clear pattern to salinity and the interpretation of $\delta^{13}C_{foram}$ may be difficult.

7.2.2 Sediment core data from Loch nan Corr

The results from the new core collected from LNC are presented in Figure 7.7, alongside a summary of the foraminiferal fauna from the nearby core investigated by Lloyd (2000). Correlation between these cores is based on lithostratigraphy and also on foraminiferal spot samples from the new core. Foraminiferal data exist throughout the marine and brackish section of the original core (Figure 7.7). However, isotope analysis is restricted to the lower 2 m of the new core due the paucity of calcareous tests in the remainder of the new core. Nevertheless, the calcareous tests do span the salinity boundary from the marine to brackish environment previously identified by Lloyd (2000). See Chapter 5 for full details of core correlations.

In total, 21 samples were measured for oxygen and carbon isotope ratios (Figure 7.7). The core has been divided into zones based upon the foraminiferal summary diagram (Lloyd, 2000).

Oxygen isotope ratios from foraminifera

The contemporary data show that marine and freshwater $\delta^{18}O_w$ are isotopically very distinct from one another and temperature has a minimal effect. If the same relationship between $\delta^{18}O_{foram}$ and salinity exists, then Zone 1 should have relatively high $\delta^{18}O_{foram}$, followed by a gradual decline across Zone 2 and 3 due to a reduction in marine (salinity) influence.

Zone 1

The basal value of Zone 1 is very low, between 713 cm to 660 cm, $\delta^{18}O_{foram}$ is 0.73‰. Up through Zone 1, $\delta^{18}O_{foram}$ values increase to around 1.2‰, but then drop to 1‰ at the top of the zone (633 cm). This appears to correspond with the general trend in the biological reconstruction (Lloyd, 2000).

Zone 2

The drop in values is followed by a progressive increase in $\delta^{18}O_{foram}$ across Zone 2, to a peak of 1.4‰ at 561 cm. $\delta^{18}O_{foram}$ values remain the same as the majority of the values are in error of each other (0.1‰) across Zone 2. The isotope data do not support the trend identified in the faunal data in Zone 2, as $\delta^{18}O_{foram}$ values do not decline over the zone.

Zone 3

Zone 3 is characterised by a single value, which records a decrease in $\delta^{18}O_{foram}$ values from the top of Zone 2, at 521 cm $\delta^{18}O_{foram}$ is 0.8‰. This could be interpreted as $\delta^{18}O_{foram}$ representing less saline conditions, corresponding with the foraminiferal reconstruction.

Carbon isotope ratios from foraminifera

The contemporary data show there is not a strong relationship with salinity

Zone 1

At the base of Zone 1, the $\delta^{13}C_{foram}$ values increase from –0.96‰ to 0.28‰ between 633-625 cm. This appears to follow the general trend in the biological reconstruction (Lloyd, 2000).

Zone 2

Carbon isotope ratios remain high across the boundary with Zone 2, to 609 cm except for an isolated low value (–0.89‰) at 681 cm. The basal section of Zone 2 contains the highest $\delta^{13}C_{foram}$ values recorded from the core. Values then become progressively lower and peak at –1.71‰ at 561 cm. Values then fluctuate around –1.4‰ to –1.5‰. This appears to follow the general trend in the biological reconstruction (Lloyd, 2000) but the shift to lower values with Zone 2 occurs rapidly compared to the gradual shift in the faunal diagram.

Zone 3

Zone 3 records a single value of –1.31‰, similar to Zone 2.

7.3 Discussion

The $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ do not show a very clear correlation with the summary foraminiferal salinity reconstruction (Figure 7.7). As $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ do not co-vary with each other ($R^2 = 0.04$, Figure 7.8), this implies that they are not responding to a common environmental variable.

7.3.1 Oxygen isotope ratios from foraminifera

The $\delta^{18}O_{foram}$ changes do not correlate with changes in the biological salinity reconstruction (Lloyd, 2000). For example, $\delta^{18}O_{foram}$ values across Zone 1 and Zone 2 can be interpreted as remaining stable or slightly increasing when the foraminiferal salinity reconstruction suggests the basin is becoming less saline (Lloyd, 2000). If the $\delta^{18}O_{foram}$ were related to salinity, $\delta^{18}O_{foram}$ values would be expected to lower due to the influence of lighter $\delta^{18}O_w$ freshwater entering a basin. Possible explanations for the unexpected trend in $\delta^{18}O_{foram}$ signal are the insensitivity of the technique to salinity and micro-habitat.

Insensitivity of Oxygen isotope ratios from foraminifera to salinity

$\delta^{18}O_{foram}$ are insensitive to changes salinity changes (i.e. ~6 psu) between brackish and marine environments. There is an overlap between $\delta^{18}O_w$ data from RTP and Craiglin Lagoon, samples taken at 25 psu (brackish water) are within error at 2 sd (0.2‰) with samples taken at 32 psu (marine water). This means a large difference in salinity >5 psu will result in a small change around –0.1‰ shift in $\delta^{18}O_w$ and inturn $\delta^{18}O_{foram}$. It is possible that salinity only changed by around ~6psu between Zone 1 and 2. If this occurred, it is unlikely that $\delta^{18}O_{foram}$ is sensitive enough to identify this change in environment. As $\delta^{18}O_{foram}$ analyses were not taken from the most marine section (identified by the foraminiferal reconstruction) of the core between 673 to 633 cm (i.e. the break in analysis because the sediment was devoid of *H.germanica*), it is possible the remaining sections of Zone 1 and Zone 2 were not significantly more or less saline than one another, which prevented $\delta^{18}O_{foram}$ recording any significant change in values. This explanation seems likely as the contemporary $\delta^{18}O_w$ provides supporting evidence.

Vital effects / Species –specific effects

Micro-habitat changes in carbonate ion concentrations [$CO^{2-}{}_3$] in pore-waters can affect the $\delta^{18}O$ and $\delta^{13}C$ signal of infaunal species without affecting the faunal composition (Bemis *et al.*, 1998; Spero *et al.*, 1997). *H.germanica* is an infaunal species (Murray, 1979) and therefore probably assimilates $\delta^{18}O$ from the ambient sediment pore-water, and could be influenced by variations in [$CO^{2-}{}_3$]. If the pH of pore-water is low the [$CO^2{}_3{}^-$] concentration will decrease, causing a mild ^{18}O enrichment in $\delta^{18}O_w$ causing $\delta^{18}O_{foram}$ values to remain high instead of decreasing (Bemis *et al.*, 1998). During an isolation event, the pH of basins is known to change (Seppå *et al.*, 2000). However, it is unlikely that changes in [$CO^2{}_3^-$] are responsible for maintaining the high $\delta^{18}O_{foram}$ values seen in Zone 2. Research suggests that changes in [$CO^2{}_3^-$] would result in $\delta^{13}C_{foram}$ covarying with the $\delta^{18}O_{foram}$ (Spero *et al.*, 1997). The isotope data do not support such a trend.

Opportunistic strategies

Changes in the time of calcite precipitation could affect the $\delta^{18}O_{foram}$ signal. Foraminifera will precipitate calcite when the environmental conditions are most favourable (opportunistic strategies). The two dominant factors that control calcite precipitation are oxygen content and nutrient supply (Van der Zwaan *et al.*, 1999). If a brackish basin is stratified during the spring and summer, the oxygen content can become restricted, preventing calcite precipitate until the early autumn after the basin waters have overturned and reoxygenated. If autumn is when optimum conditions are created for calcite precipitation, isotopic fractionation will occur when the temperature of the basin is cooler. The limited contemporary data from the Craiglin Lagoon shows autumn basin water temperatures are lower than in the summer (Figure 7.5a). Foraminifera precipitating calcite in warmer temperatures will be isotopically lower than foraminifera which have precipitated at lower water temperatures (–0.24‰/°C). This could explain the relationship of the $\delta^{18}O_{foram}$. However, this needs to be verified by extensive contemporary observations from marine and brackish isolation basins. The ecological information for *H.germanica* is limited and it is unknown when the species precipitates carbonate.

7.3.2 Carbon isotope ratios from foraminifera

The contemporary data suggests that $\delta^{13}C_{foram}$ will not be related to salinity or temperature, the $\delta^{13}C_{foram}$ data from LNC appears to show this. The overall $\delta^{13}C_{foram}$ signal is from an isotopically high to lower composition over the marine brackish boundary. This trend could be interpreted as $\delta^{13}C_{foram}$ responding to a decrease in basin salinity. However, the rapid shift in $\delta^{13}C_{foram}$ values within Zone 2 does not follow the *gradual* change in faunal trend. This implies that $\delta^{13}C_{foram}$ is not related to salinity. A range of explanations are discussed to assess their likely effect on $\delta^{13}C_{foram}$ values.

Changes in the source of organic carbon

Lloyd and Evans (2002) suggested changes in the source of organic carbon could be the main controlling variable for $\delta^{13}C_{foram}$. As the salinity of the basin changes the source of organic carbon is expected to change (see Chapter section 2.4). The $\delta^{13}C_{org}$ values from Zone 1 are interpreted as deriving from marine algae and aquatic plants. Zone 2 and 3 record values from –22‰ to –24‰ (Figure 7.7), which is interpreted as brackish sediment, comprising a mix of terrestrial, freshwater and marine aquatic sources. This implies an increase in organic material from terrestrial sources during Zone 2. An increase in terrestrial organic matter will enrich the $\delta^{13}C_{TDIC}$ in ^{12}C, causing $\delta^{13}C_{foram}$ to decrease. If the $\delta^{13}C_{foram}$ responded to changes in carbon source one would expect a strong correlation between $\delta^{13}C_{foram}$ and $\delta^{13}C_{org}$. No relationship is found ($R^2 = 0.02$, Figure 7.9). The lowest $\delta^{13}C_{org}$ corresponds with the highest $\delta^{13}C_{foram}$ values (Figure 7.7). Therefore, changes in the source of organic carbon are not the controlling variable of $\delta^{13}C_{foram}$, values in LNC.

Micro-habitat effects

Alternatively, the decrease in $\delta^{13}C_{foram}$ values within Zone 2 could be associated with a microhabitat effect. *H.germanica* is an infaunal species (adapted for survival in low-oxygenated environments) (Murray, 1979). *H.germanica* assimilates $\delta^{13}C$ from the ambient sediment pore-water, which could be different from the isotopic composition of the basin water. It is likely that decomposition of this organic rich matter could result in the release of ^{12}C enriched CO_2 to the sediment pore-water (Woodruff *et al.*, 1980; Belanger *et al.*, 1981; Grossman, 1984, 1987; McCorkle *et al.*, 1990). This directly influences the $\delta^{13}C_{foram}$ because foraminifera will preferentially take up the isotopically lower ^{12}C. The shift to depleted $\delta^{13}C_{foram}$ values coincides with an increase in TOC, suggesting the sediment was organically rich compared to the sediment in Zone 1. TOC increase from 5 to 10 % between Zone 1 and Zone 2 (Figure 7.7). Langer *et al.* (1995) suggested the influence of micro-habitat effects to be responsible for depleted $\delta^{13}C$ values from semi-infaunal species living within low-oxygenated organic rich sediment in Madang Lagoon, Papua New Guinea. The foraminifera displayed significantly lower values compared to the same species in less organically rich sediment. A similar trend was found with infaunal species from the Southern California Borderlands (Grossman, 1984). The pore-water was found to be 2.7‰ lower compared to the $\delta^{13}C$ TDIC (Grossman, 1984). Extensive data from brackish and marine basins needs to be collected with measurements on pore-water $\delta^{13}C_{TDIC}$, as well as isotopic analyses on a range of infaunal and epifaunal species to test if this scenario can exist within Scottish isolation basins.

7.4 Summary

1. The lack of contemporary foraminifera at RTP and Craiglin Lagoon prevented the assessment of the relationship between foraminifera - salinity and temperature. The contemporary $\delta^{18}O_w$ data shows a clear relationship with salinity. Marine and freshwater are isotopically very distinct and temperature appears to have a minimal effect but may become complicated during brackish phases. The $\delta^{13}C_{TDIC}$ data are not influenced by salinity or temperature.

2. The $^{18}O_{foram}$ and $\delta^{13}C_{foram}$ signal from LNC do not follow the broad trends in the biological salinity reconstruction, in particular during the main brackish phases of the isolation of the basin (Zone 2). The reason why is not readily understood. A number of possible explanations were explored to determine

the controlling variable of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$, especially during brackish phases. It is likely that $\delta^{18}O_{foram}$ is insensitive to small changes in salinity which may have characterised the faunal data from Zone 1 and Zone 2. This study has shown that $\delta^{13}C_{org}$ is not the controlling variable for $\delta^{13}C_{foram}$ values within LNC as speculated by Lloyd and Evans (2002). The strong link between $\delta^{13}C_{foram}$ values and TOC suggest that micro-habitat effects could be responsible. However, it is possible that a combination of factors influence the $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ signal during brackish phases.

3. Overall, this study highlights $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ from *H.germanica* are not suitable proxies for palaeosalinity reconstruction within isolation basins. This highlights the need for further research from contemporary environments to asses the influence of salinity, micro-habitat effects, changes in precipitation patterns and temperature. Moreover, detailed ecological information about foraminiferal calcite precipitation requirements are needed before accurate interpretations of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ from isolation basins can be made.

Chapter 8

The application of $\delta^{18}O_{diatom}$ as a palaeosalinity proxy

8.1 Introduction

This chapter will present the results of $\delta^{18}O_{diatom}$ analysis of Upper Loch Nan Eala (ULNE), Arisaig (Figure 3.2) as an indicator of palaeosalinity change within a fossil isolation basin. The application of $\delta^{18}O_{diatom}$ as a palaeosalinity indicator is a novel use of the proxy which has traditionally been used as a palaeotemperature indicator in carbonate-poor marine sediments (Clayton *et al.*, 1972; Julliet-Leclerc and Labeyrie, 1987, Matheney and Knauth, 1989; Shemesh *et al.*, 1992, 1995; Brandriss *et al.*, 1998; Schmidt *et al.*, 2001). More recently $\delta^{18}O_{diatom}$ has been applied to lacustrine sediments as a tool for reconstructing changes in hydrological conditions (Leng *et al.*, 2001; Barker *et al.*, 2001; Rioual *et al.*, 2001) and temperature and isotopic composition of precipitation (Shemesh and Peteet, 1998; Rosqvist *et al.*, 1999; Hu and Shemesh, 2003; Jones *et al.*, 2004; Rosqvist *et al.*, 2004). $\delta^{18}O_{diatom}$ has never been applied to marginal marine settings nor has it been used as a salinity indicator. The $\delta^{18}O_{diatom}$ signal should be controlled by three main factors; water salinity (ambient isotopic concentration of the water), temperature and possibly vital effects at the time of silicate secretion (Brandriss *et al.*, 1998). Isolation basins in NW Scotland that are influenced by meteoric water will receive inputs of isotopically lower (<–6.5‰) (Darling *et al.*, 2004) water than the ocean water (0‰) (Hoefs, 1987). The greater the freshwater influence into an isolation basin the more negative $\delta^{18}O_{diatom}$ values will become.

As with the other isotope palaeosalinity proxies tested in Chapters 6 and 7, samples from contemporary isolation basins were collected and used to interpret down-core results. However, before $\delta^{18}O_{diatom}$ measurements could be undertaken, an extraction technique for the proxy was developed.

8.2 Results

8.2.1 Extraction technique

A sample with a minimum of 5 mg of pure diatom material is needed for $\delta^{18}O_{diatom}$ analysis because the analytical method (fluorination technique) liberates oxygen from all material in the samples, such as diatoms, clay, silt, pollen and carbonate. Previous researchers used a combination of filtering, ultrasonic washing, settling and decanting procedures (Labeyrie, 1974). Shemesh *et al.* (1995) used a combination of the above methodology with the addition of a heavy liquid separation to extract sufficient diatom frustules for analysis. Due to the variable organic and minerogenic content of isolation basin sediments, a rigorous technique was needed to isolate pure diatom frustules (with a level of contamination of less than 4% clay and silt) from all types of sediment found within isolation sequence. Based on previous work a, extraction procedure was developed.

The density separation technique for isolating rhyolitic tephra shards (Turney, 1998) was successfully adapted for extracting diatoms from isolation basins (see Chapter 5 for the detailed description). After a standard diatom preparation technique, where organic and carbonate material was removed by standard chemical treatment (Battarbee *et al.*, 2001), the samples were sieved through a 15-63µm sieve mesh to remove detrital clay, silt and sand particles. The size of the sieve mesh was chosen after measuring the average size range of the fossil diatoms from ULNE. It was discovered that the relative density of 2.2 gcm^3 was the optimal density for separating diatoms from clay and silt material from ULNE. Figures 8.1a-c illustrates the difference between the 2.2 gcm^3 "float" and 2.3 gcm^3 "float". The method was capable of isolating a range of species types of varying size.

8.2.2 Contemporary samples and sediment core data from ULNE

Contemporary data

As discussed in Chapter 7, $\delta^{18}O_w$ shows a clear relationship with salinity. The $\delta^{18}O_w$ values are more negative with low salinity concentrations. The $\delta^{18}O_w$ values range from 0.2‰ to –1.7‰ for marine waters from Rumach Tidal Pond. They range from –0.9‰ to –1.9‰ for brackish waters (Craiglin Lagoon) and are around –6.6‰ in freshwater from Loch Nan Corr (LNC). The difference between fresh and marine environment is around 5‰. However, overlap in $\delta^{18}O_w$ values does occur between the brackish and marine analogue (Figure 7.1a). Nevertheless, it suggests if $\delta^{18}O_{diatom}$ secrete their silica in isotopic equilibrium with basin water, $\delta^{18}O_{diatom}$ values would be related to salinity.

While the extraction technique successfully extracted diatomite from sediment cores, I was unsuccessful in isolating pure diatomite from the surface sediment of the three contemporary basins. Also insufficient material was collected using a plankton net. This prevented a mixing line being developed to establish the relationship between $\delta^{18}O_{diatom}$ and salinity or temperature. Nevertheless an extensive literature search provided a range of end-member values so fields of marine and lacustrine $\delta^{18}O_{diatom}$ values could be constructed (Table 8.1). Table 8.1 and Figure 8.1a was constructed using a combination of contemporary and fossil samples because limited contemporary data exists within the literature. The data plot into two main groups, although overlap occurs between the two end-member fields, possibly because of the range of analytical procedures employed and the diverse range of environments from which samples have been taken (Mediterranean lakes to the Southern Ocean).

Table 8.1 and Figure 8.2 show the range of values from marine and freshwater samples: typically marine samples are >30‰ (full range from 29‰ to 47‰) and freshwater samples are <33‰ (full range 16‰ to 33‰). The full range of contemporary marine samples is 29‰ to 43‰, the fossil marine samples range from 36‰ to 47‰ (Table 8.1, Figure 8.2). The contemporary freshwater range is only based upon three samples. However, the fossil freshwater range confirms the contemporary results that freshwater values are typically less than 32‰. The fossil freshwater values range from 16 to 33‰ (Figure 8.2).

The Upper Loch nan Eala (ULNE) sediment core

Sediment was successfully extracted from Lateglacial and Holocene marine, brackish and freshwater sections from ULNE. However, very few samples were isolated from the Holocene marine section. The clay content of this section increased to >20% and so numerous samples from this section contained a high mix of clay and silt with the diatoms. The density of the separating medium was adjusted to 2.1 – 2.0 gcm^{3-} to see if the clay had a similar relative density to the diatoms, but little or no improvement was seen.

Figure 8.3 illustrates the down core profiles of $\delta^{18}O_{diatom}$ and $\delta^{13}C_{org}$, plotted alongside the diatom salinity summary by Shennan *et al.* (1994). The results are described in relation to the seven main zones, based upon the diatom flora (Shennan *et al.*, 1994) and $\delta^{13}C_{org}$ data discussed in Chapter 6. Figure 8.4 illustrates the relationship between the end-member fields identified in Figure 8.2 and the ULNE data.

Zone 1 – Marine Lateglacial

According to the diatom flora, Zone 1 records marine conditions during the Lateglacial (Shennan *et al.*, 1994). Unfortunately, it was difficult to extract pure diatom samples from this section and so only five samples were analysed. A broad range of $\delta^{18}O_{diatom}$ values were recorded through this zone from 10‰ at the base to 30‰ at the top of the zone (Figure 8.3). The majority of the

$\delta^{18}O_{diatom}$ data from Zone 1 plots within the freshwater range but there is a minor overlap with the marine range (Figure 8.4). In this zone, isotope data do not mirror the trend in the biological salinity reconstruction.

Zone 2 – Freshwater loch

The diatom flora record a transition to a freshwater environment due to a RSL fall (Shennan *et al.,* 1994). The $\delta^{18}O_{diatom}$ values in this zone are higher than in Zone 1 (Figure 8.3). The $\delta^{18}O_{diatom}$ records values between 31‰ to 40‰ but average $\delta^{18}O_{diatom}$ values are around 38‰ when the value at 567cm is excluded. The sample at 567 cm is excluded because it appears to be an outliner, it had a value of 31‰ which detracts from the general trend seen within Zone 2 (Figure 8.3). The majority of the $\delta^{18}O_{diatom}$ values from this zone plot within the marine range, expect for the sample at 567 cm which plots within the freshwater range (Figure 8.4). Overall, the isotope data do not mirror the trend in the diatom salinity reconstruction (Shennan *et al.,* 1994).

Zone 3 – Brackish environment

The diatom flora suggests the marine influence to ULNE increased to create brackish conditions in this zone (Shennan *et al.,* 1994). Pure diatomite was extracted from 13 intervals across this zone, making it one of the best sampled zones in the core. The $\delta^{18}O_{diatom}$ values range from 27‰ to 37‰, however, the sample at 500 cm appears to be an outlier (27‰) because the majority of the samples have values between 34‰ to 37‰ (Figure 8.3). The majority of the $\delta^{18}O_{diatom}$ values from Zone 3 plot within the marine range, however, two of the values plots within the overlap of the marine and freshwater ranges Figure 8.4. Overall, the isotope data from Zone 3 do not mirror the trend in the biological salinity reconstruction (Shennan *et al.,* 1994).

Zone 4 – Holocene marine

The diatom flora suggests the marine influence to ULNE increased over this zone to create marine conditions (Shennan *et al.,* 1994). Zone 4 (average value around 27‰) shows a clear difference in $\delta^{18}O_{diatom}$ values compared to Zone 3 (34‰). The $\delta^{18}O_{diatom}$ values are significantly depleted compared to Zone 3 and cluster around 25‰ (Figure 8.3). All the $\delta^{18}O_{diatom}$ values plot within the freshwater field of Figure 8.4. The isotope data from Zone 4 do not mirror the trend in the biological salinity reconstruction (Shennan *et al.*, 1994).

Zone 5 to 6

No samples were analysed from Zone 5 or 6. The extraction technique could not separate diatomite from silt and clay material successfully. A number of samples contained a mix of white diatom bands with brown silt/clay material intermixed within the samples after sieving and separating with SPT (relative density 2.2 gcm^3). Despite attempts to adjust the density of the SPT from 2.2 to 2.1 and 2.0 gcm^3 to try and isolate the diatomite from the silt and clay, samples were still considered too contaminated with detrital material to be analysed.

Zone 7 – freshwater loch and infilled basin

Only three samples were analysed from this zone because the material at the top of the zone becomes very fibrous due to peat formation created by the infilling of the basin, which prevents diatom accumulation. The $\delta^{18}O_{diatom}$ values range from 31‰ to 36 ‰ (Figure 8.3). These values are greater by 5‰ to 10‰, compared to the marine samples from Zone 4. The $\delta^{18}O_{diatom}$ values from this zone are comparable with values from Zone 2 and 3. The $\delta^{18}O_{diatom}$ values from Zone 7 plot within the marine range and the overlap between the fresh and marine ranges defined by the published data (Figure 8.4). The isotope data from Zone 7 do not mirror the trend in the biological salinity reconstruction (Shennan *et al.*, 1994).

8.3 Discussion

The aim of measuring $\delta^{18}O_{diatom}$ was to test if the proxy could be used as an alternative palaeosalinity indicator. It was expected that lower $\delta^{18}O_{diatom}$ values would be related to reduced salinity phases previously identified in the diatom flora (Shennan *et al.,* 1994). The isotope data from ULNE do not support biological reconstruction. The $\delta^{18}O_{diatom}$ data from ULNE are complex and a meaningful trend is hard to identify. When the data from ULNE are compared with marine and lacustrine end-member fields, the results are generally the reverse of the expected pattern. The values from the marine zones plot within the freshwater field defined in Figure 8.4. The Lateglacial marine samples are significantly lower than the marine Holocene samples. The samples from Zone 3 plot with the marine field of Figure 8.4. The diatom reconstruction (Shennan *et al.,* 1994) suggests this is a brackish/ marine environment. Based on the biological reconstruction, it would be expected that the isotope values would form an intermediary zone between the marine and freshwater end-member fields. As the majority of the samples from Zone 3 plot well within the marine field, this suggests that the $\delta^{18}O_{diatom}$ are not reflecting brackish water conditions. There are at least five possible reasons for the discrepancy between the ULNE data and the end-member fields:

1. *Samples were contaminated by clay and silt grains.* A recent study by Morley *et al.* (2004), published after my laboratory work was completed, used a similar cleaning technique to the one employed in this thesis. Morley *et al.* (2004) proposed a 4 stage cleaning method for lacustrine sediment that can purify samples of diatom silica from detrital material. Stage 1: organic and carbonate removal; by standard chemical procedures, Stage 2: sieving samples; Stage 3: Differential settling; Stage 4: STP separation. The method employed in this study is similar except for Stage 3, which was omitted. Stage 3 involves repeated centrifuging of the sieved fraction with water. Centrifuging causes stratification to occur between the denser silt or coarser particles and the diatoms. The white diatom bands are then carefully pipetted off. The process is repeated several times until no diatom bands remain. This step was found crucial for isolating diatoms when large amounts of the

clastic material were present, especially if the clastic material was similar in size to the diatoms being extracted. Morley found the samples with the greatest clay/silt concentrations had the lowest $\delta^{18}O_{diatom}$ values of around +10‰. Therefore, the amount of clay and silt left remaining in a sample will significantly affect the $\delta^{18}O$ signal. The Morley study strongly suggests that contamination by clay and silt grains is a likely explanation for the lowering of marine values away from their expected values. Also, it might explain lack of success in extracting many samples suitable for analysis from the Holocene marine section of ULNE and those contemporary isolation basin surface sediments with high silt contents (Bendle, 2003).

1. *The samples were contaminated by sodium polytungstate residue.* Morley *et al.* (2004) showed that samples contaminated with SPT will have a lower than expected $\delta^{18}O_{diatom}$ signal by around 6.5‰. SPT is notoriously difficult to remove from samples (Turney, 1998) and it is typically removed by centrifuging the sample at least 3 times with distilled water. Morley found the best method to remove the SPT was by rinsing samples over a 10μm sieve after centrifuging the samples 3 times because centrifuge washing alone was insufficient to remove SPT. I did not rinse samples over a 10μm sieve but washed the samples at least 4 or 5 times to overcome the problem of SPT contamination. As the samples in this study were not rinsed over a 10μm mesh after centrifuge washing, the potential for sodium polytungstate contamination is a real possibility.

3. *Vital effects*, related to species size, can affect the $\delta^{18}O_{diatom}$ signal. Shemesh *et al.* (1995) found there was a 0.2‰ difference between the large and small marine diatoms analysed for $\delta^{18}O$ ratios. However, this result was considered insignificant. Brandriss *et al.* (1998) repeated the study using freshwater diatoms and managed to reproduce this offset.

As this result is reproducible it suggests that differences in species vital effects are real, even though they are small. The degree of offset between the two groups is too small to account for the degree of isotopic shift between the expected marine and freshwater values. Fractional offsets to salinity might be species specific, causing bulk samples to mask the true relation of the samples to salinity. Brandriss *et al.* (1998) reported that different diatom species, fractional offset to temperature were similar. This is an encouraging result for the use of bulk samples. However, in marginal marine settings where the range of environmental variables are highly changeable compared to the open ocean it is unknown if mono-specific samples would produce the same result as bulk diatom samples. Hence, further research is required to establish if mono-species vs. bulk $\delta^{18}O_{diatom}$ samples, living in a marginal marine setting, record similar $\delta^{18}O_{diatom}$ values as open marine samples.

4. *Diagenetic processes overprinting the original $\delta^{18}O$ signal.* A number of studies suggest that the $\delta^{18}O_{diatom}$ signal may be acquired after the diatoms have been deposited in the sediment. Schmidt *et al.* (1997) found that fossil (sedimentary) diatoms were higher by 3‰ to 10‰ compared to "living" marine diatoms collected from plankton tows from high-latitude oceans and cultured diatoms. It was speculated that this was because of secondary re-equilibrium with ^{18}O enriched pore waters in the sediment column (Schmidt *et al.*, 1997). Brandriss *et al.*, (1998) conducted a series of experiments on living freshwater diatoms and found a similar offset between his results and values from fossil diatoms in the literature. Schmidt *et al.* (2001) substantiated this hypothesis by conducting a series of flow-through experiments, using cultured marine diatom species, to study dissolution kinetics under controlled conditions. Schmidt *et al.* (2001) suggests secondary isotopic exchange reactions occur after the diatoms are deposited in the sediment. Dissolution not only affects the hydroxl outer layer but also the internal framework layer

(Si-O-Si). Slow internal condensation processes causes silica to be precipitated resulting in $\delta^{18}O_{diatom}$ values becoming enriched by pore-water ^{18}O. It is unknown if this would occur to samples from marginal marine environments, as all the research has compared results from cultured diatoms (which should be analytically very pure) with marine samples from the open ocean. Isolation basin sediments are subject to changes in pH levels and redox fronts after deposition. This results in carbonate and diatom dissolution and so sections of some sites have very poor diatom abundance (e.g. Loch nan Corr). Diagenetic processes might explain the enrichment of the freshwater diatoms extracted from the freshwater sections of ULNE (Zones 2 and 7). However, I would also expect marine samples to be affected by diagenetic processes. A trend towards higher values is not observed, which implies diagenetic alteration is not responsible for $\delta^{18}O_{diatom}$ values in Zones 1 and 4. Detailed further research needs to be undertaken on sediment from different environments to establish how and when the $\delta^{18}O_{diatom}$ signal is acquired. Until this is known this explanation for the anomalous results in Zone 2 and Zone 7 remains speculative.

5. *Meltwater.* Three samples from the Lateglacial marine section of ULNE record (Zone 1) have exceptionally light values (around 10‰) compared to the Holocene marine samples from Zone 4 (34‰ to 27‰). Meltwater is isotopically lower relative to normal marine water because it contains a greater amount of freshwater, which would in turn influence the $\delta^{18}O_{diatom}$ signal. This interpretation is only based upon three samples and there is no additional evidence to support the occurrences of meltwater influencing the basin at this particular point in time. Therefore, it is extremely speculative that meltwater is a possible explanation for the anomalous $\delta^{18}O_{diatom}$ values.

As detrital or chemical contamination causes a lowering of $\delta^{18}O_{diatom}$ value of c. 6.5‰ to 10‰ (Morley *et al.*, 2004), contamination by detrital clay silt or SPT residue is the most likely cause of spurious results from the marine zones of ULNE because the clean-up procedure used was not as rigorous as the one devised by Morley *et al.* (2004). While the detrital contamination causes the lowering of $\delta^{18}O_{diatom}$ values, an alternative explanation must be sought to explain the enriched $\delta^{18}O_{diatom}$ values from the freshwater samples. It is possible that diagenetic processes are responsible and $\delta^{18}O_{diatom}$ values are reflecting pore-water $\delta^{18}O$. However, secondary diagenetic processes are not fully understood. Schmidt *et al.* (2001) comments that 'controls on biogenic silica dissolution and preservation in various sedimentary environments are complex and their effects on the evolution of the isotopic signature are not yet understood', suggesting this aspect of $\delta^{18}O_{diatom}$ research requires further investigation before the $\delta^{18}O_{diatom}$ signal can be interpreted with increased confidence.

8.4 Conclusion

The results suggest $\delta^{18}O_{diatom}$ from isolation basin sediments cannot be used as a palaeosalinity proxy. No meaningful trend was established from the data of ULNE. The reason why is not readily understood, especially for the freshwater diatom samples but the likely explanation is that the samples were adversely affected by detrital clay and silt or SPT contamination, causing $\delta^{18}O_{diatom}$ to be unrelated to salinity trends identified by diatom flora (Shennan *et al.*, 1994). The results imply that the cleaning technique developed was inadequate and requires further refinement. Since this study was undertaken, advances in diatom cleaning techniques have occurred (Morley *et al.*, 2004; Leng *pers. comm.*). A rigorous 4 stage cleaning technique has been developed for lacustrine sediments (Morley *et al.*, 2004). The 4 stage method has successfully been applied to lacustrine sediments from Lake Baikal (Holocene and Eemian samples) and Lochnagar in the Scottish Cairngorms (Holocene samples). The addition of a stage that involved repeated settling of the samples and a more rigorous cleaning procedure employed for the removal of SPT from diatom 'floats' would have resulted in cleaner diatom fractions being isolated and more samples being analysed from ULNE. As this method separates diatoms without the need for SPT the potential for chemical contamination is eliminated (Leng *pers. comm.*). To establish if the cleaning procedure employed in this thesis was the cause of the spurious results from ULNE would require the study to be repeated using the Morley *et al.* (2004) 4 stage method.

Despite the negative results from this study $\delta^{18}O_{diatom}$ values could in theory still be successfully applied as an alternative isotope proxy for salinity reconstructions, if one of the new cleaning procedures was applied. However, in order to establish if $\delta^{18}O_{diatom}$ values are related to salinity trends in isolation basins, a comprehensive study of $\delta^{18}O_{diatom}$ values in contemporary isolation basins is needed. For example, measurements of water temperature, salinity, stable isotope ratio from basin water and pore-waters will enable the factors controlling $\delta^{18}O_{diatom}$ in isolation basins to be identified. Diatoms collected from sediment traps and surface sediments should be compared to study the effects of dissolution and secondary digenesis. Experiments comparing monospecific and bulk sample results also warrant further investigation.

Chapter 9

The application of biogenic silica and total organic carbon as a proxy for palaeoenvironmental reconstruction from fossil isolation basin records

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9.1 Introduction

One of the aims of this thesis is to investigate if additional environmental proxies, other than salinity indicators, are contained within isolation basins sediments. The use of fossil isolation basin sediments as records of palaeoenvironmental change has received little attention, despite a few earlier studies (e.g. Birks, 1973; Thompson and Wain-Hobson, 1979; Shennan *et al.*, 1996b; Lloyd and Evans, 2002). As isolation basins are marginal marine environments, they provide a crucial link between the terrestrial and marine realm. Isolation basin sediments are potentially extremely valuable palaeoenvironmental archives of land-ocean interactions. Chapter 2 outlined the use of biogenic silica ($BSiO_2$) and total organic carbon (TOC) analysis as proxies of palaeoenvironmental change. $BSiO_2$ is a measure of aquatic productivity that is predominantly formed by diatoms and is assumed to reflect air temperatures in lacustrine environments (Coney, 1988). This has been confirmed by contemporary observations from lakes (Schindler *et al.*, 1990). A number of studies from lacustrine and marine environments have shown that changes in aquatic productivity are phased linked to changes in regional and global palaeoclimate (e.g. Kaplan *et al.*, 2002; Wagner *et al.*, 2000; Harris *et al.*, 1996; Colman *et al.*, 1995; Matthewson *et al.*, 1995). For example, both Kaplan *et al.* (2002) and Wagner *et al.* (2000) reconstruct major trends in Holocene climate from lake records in southwest and east Greenland.

Research by Colman *et al.* (1995) and Matthewson *et al.* (1995) identified glacial-interglacial cycles from Lake Baikal and marine cores off Northwest Africa using $BSiO_2$. TOC will also be used as a secondary measure to estimate carbon productivity. TOC is the measure of total terrestrial and aquatic carbon productivity and is commonly used in conjunction with $BiSO_2$ (e.g. Wagner *et al.,* 2000). This chapter examines if trends in the $BSiO_2$ and TOC recorded from two different types of isolation basin sequences Loch nan Corr (LNC) and Upper Loch nan Eala (ULNE) are related to palaeoclimate events during the Lateglacial and the Holocene (Figure 3.2 and 3.21). LNC contains an extended Holocene isolation sequence where the salinity changes were slow because LNC took over 6000 years to isolate (Lloyd, 2000; Lloyd and Evans, 2002). In contrast, ULNE records Lateglacial and Holocene RSL history and changes in salinity occurred rapidly across each isolation contact. The $BSiO_2$ and TOC signals from each site are compared to the regional North Atlantic palaeoclimate record from the GRIP ice core, local events identified in peat and speleothem and ocean records from around the UK.

9.2 Results

Age/depth models have been created for the new cores from LNC and ULNE. The models were developed using a series of AMS calibrated radiocarbon measurements transposed from the original cores (from which biological palaeosalinity reconstruction were created (Lloyd, 2000; Shennan *et al.,* 2000)) to the equivalent stratigraphic levels in the new cores (see Chapter 6 for details of core correlations).

Loch Nan Corr sediment core

Figure 9.1 presents the profiles of C/N ratio, particle size, TOC and $BSiO_2$ against the summary of the foraminiferal fauna palaeosalinity reconstruction (Lloyd, 2000) from LNC. Correlations between the two cores are based upon major lithostratigraphic boundaries and foraminiferal spot samples from the new core (see Chapter 6 for details). The core from this study has been split into three main zones (marine, brackish and freshwater) based upon the foraminiferal reconstruction (Lloyd, 2000).

Zone 1 – Marine

Zone 1 is characterised by low $BSiO_2$ and TOC values; $BSiO_2$ is between 0.4 – 0.8% and TOC 5%. C/N ratios vary between 9 – 14. The sediment is composed of 50% sand and 25% silt and clay.

Zone 2 Brackish basin

Zone 2 shows a clear difference in $BSiO_2$ and TOC values from Zone 1. $BSiO_2$ remains low (0.4% to 0.9%) until 569 cm, after which $BSiO_2$ levels increase to a peak of 4.5% at 481 cm. Other prominent peaks are seen at 401 cm (4%) and 313 cm (3%). This is followed by a gradual decline in values to a low of around 0.3% at 175 cm. Values increase to 1.2% at the top of the zone (137 cm) (Figure 9.1).

The TOC shows a similar trend to $BSiO_2$. TOC values gradually increase from 5 to 10% between 609 cm to 569 cm. However, this rise in TOC values occurs before the rise in $BSiO_2$ data. TOC values remain high around 7% to 13% until 241 cm. From this point, TOC fluctuates between low values of <1% to peaks up to 15%. Prominent peaks are seen at depths of 201 cm (7%) and 137 cm (8%). Again this change in trend occurs at a different time to the decline in $BSiO_2$ values. The TOC decline occurs after the decline in $BSiO_2$ values (Figure 9.1).

The C/N ratios remain stable across Zone 2 with values around 15. Two troughs in values occur at 217 cm (10) and 145 cm (13) which broadly correlate with troughs in $BSiO_2$ and TOC values. The particle size concentration remains stable from Zone 1, until 265 cm. From this point the sand concentration increases dramatically from 60% to >90% by 219 cm (Figure 9.1).

Zone 3 Freshwater loch

A sharp peak in both $BSiO_2$ and TOC values occur across the transition from Zone 2 to Zone 3. $BSiO_2$ and TOC values subsequently drop to around ~0.4% and 1% respectively. The particle size concentration remains stable across the transition between the zones but C/N ratios increase to 19 (Figure 9.1).

Upper Loch Nan Eala sediment core

Figure 9.2 illustrates profiles of $BSiO_2$, TOC and C/N ratios against a diatom summary from ULNE. The most striking feature of this record is the large variation in $BSiO_2$ down core. The $BSiO_2$ and TOC data follow the overall general trend reflected in the diatom palaeosalinity reconstruction and sediment lithology. Overall, the low values in $BSiO_2$ and TOC are recorded in minerogenic sections of the core, high values in organic rich limnic sequences and intermediate values during the brackish phase. The core is split into seven zones for ease of description. The zones are based on the major changes identified in the diatom summary diagram.

Zone 1 - Lateglacial marine

In this basal minerogenic zone, both $BSiO_2$ and TOC record low values. $BSiO_2$ increases from 3% to 6% and TOC remains stable at around 6% (Figure 9.2).

Zone 2 - Freshwater loch

$BSiO_2$ and TOC show a similar trend, both dramatically increasing in values from Zone 1. $BSiO_2$ records values around 40 to 50% and TOC around 16%. $BSiO_2$ records two dips in values to 32% and18% at 609cm and 535cm at the transition between Zone 2 and Zone 3. These correlate with the two peaks in TOC values of 24% and 26%. The first peak also correlates with a peak in C/N ratios (Figure 9.2).

Zone 3 – brackish environment

This zone records intermediate values of 18% to 32% in $BSiO_2$ and high TOC values similar to Zone 2. Overall, both $BSiO_2$ and TOC decline from the base to the top of the zone (Figure 9.2).

Zone 4 – Holocene marine

There is a marked decrease in $BSiO_2$ at the boundary between Zones 3 and 4 (from 18% to 8%), then a gradual reduction to around 3%. TOC also gradually reduces from the base to the top of the core (from 12% to 3%) This trend is punctuated by a small peak in both $BSiO_2$ and TOC values to around 12% at 302 cm. There is no corresponding peak in C/N ratios (Figure 9.2).

Zone 5 – Freshwater loch

Zone 5 is characterised by a major fluctuation in TOC and C/N ratios. TOC and C/N ratios record a peak in values around 37% and 25 respectively. There is no corresponding trend in $BSiO_2$ values as they remain low around 3% (Figure 9.2).

Zone 6 – Holocene marine

$BSiO_2$ remains low with values around 5%. TOC and C/N ratio revert back to similar values recorded in Zone 4. At the top of the zone, TOC peaks to 15% but is not followed by a similar rise in $BSiO_2$ (Figure 9.2).

Zone 7 – Freshwater loch / infilled basin

The $BSiO_2$ increases at the transition between Zones 6 and 7, a peak of 18% is reached at 156 cm, which correlated with a peak in TOC of 56%. Following this peak in values, the $BSiO_2$ signal declines sharply to around 2% at the top of the core. However, the TOC and C/N ratios remain high around 54% and 25 respectively. This decline in $BSiO_2$ correlates with a change in sediment lithology from a limnic to peat sequence (Figure 9.2).

9.3 Discussion

Both LNC and ULNE record variations in $BSiO_2$ and TOC down core. However, there is a marked difference in values between LNC and ULNE. The $BSiO_2$ values for LNC (<5%) are lower compared to ULNE (5 to 55%). This sort of variation is typical of marginal marine environments. For example, the Bohai, Yellow Sea has a $BSiO_2$ content of less than 1% (Liu *et al.*, 2002). Also, lake records from east Greenland have $BSiO_2$ values around 4% (Wagner *et al.*, 2000). It is likely that the difference between LNC and ULNE is related to both the variations in diatom abundance and the amount of minerogenic matter diluting the biogenic accumulation in the basins. The pilot study (Chapter 5) showed that ULNE overall has a higher diatom abundance than LNC. However, LNC probably has a higher amount of minerogenic input into the basin. This is reflected by the difference in the TOC values from freshwater/brackish sediment between LNC and ULNE. LNC has a TOC around 10% while ULNE ranges from 20 to 50%; this suggests a higher proportion of the sediment lithology in LNC is composed of minerogenic matter compared to ULNE. I speculate that this is due to the difference in catchment relief between LNC and ULNE. LNC is surrounded by steep north and south facing slopes which will result in high minerogenic input to the lake. ULNE, in contrast, has relatively low lying relief and therefore a lower minerogenic input relative to LNC (site pictures Figure 3.10 and 3.21).

9.3.1 Loch nan Corr

Sediment physical properties

The interpretation of the $BSiO_2$ record from LNC is complicated because LNC has experienced significant changes in salinity due to RSL fall, which is shown by the foraminiferal salinity summary diagram (Figure 9.1). Several factors can influence the $BSiO_2$ record, such as salinity and climate. Thus, the interpretation of $BSiO_2$ and TOC as indirect proxies of palaeo air temperature cannot be initially assumed. It is likely that the $BSiO_2$ and TOC signals are a combination of the salinity and climate and it depends which environmental factor was dominant through time. If the $BSiO_2$ and TOC signals are related to salinity driven productivity, I would expect the lowest values to be recorded in the marine zone and the highest values in the freshwater zones with the brackish zone recording intermediary values. During fully marine conditions (Zone 1), minerogenic input would be high and cause the signals to be diluted. In addition, the marine $BSiO_2$ and TOC signals would be lower because marine waters are typically colder than freshwater (see Chapter 7, Figures 7.2). Cooler water temperatures unaffected by coastal upwelling may also have lower aquatic productivity rates relative to freshwater environments. No such correlation is found in LNC after the end of the marine phase of inundation.

The C/N profile and particle size data also suggest that $BSiO_2$ and TOC are unrelated to changes in sediment sourcing or particle size related to RSL change. The C/N ratios remain relatively stable throughout the Holocene, suggesting the high bioproduction occurred within and around the lake catchment. Even though the environmental source of organic matter may have changed (i.e. marine versus terrestrial), the relative proportion of aquatic versus terrestrial input remained stable particularly during the major changes in $BSiO_2$ and TOC records. This suggests no major input of terrestrial material into the basin, associated with RSL fall, has diluted or enhanced $BSiO_2$ and TOC signals. Changes in particle size composition have occurred down core in LNC. However, no major peak or trough in the $BSiO_2$ or TOC signals correspond with a change in particle size. For example, the major peak in $BSiO_2$ and TOC values in Zone 2 (513 to 313 cm) have a similar particle size concentration to Zone 1, where the $BSiO_2$ and TOC are lower. Thus, $BSiO_2$ and TOC values are independent of lithology changes such as particle or organic sediment sourcing. Therefore, the signals appear to be unrelated to salinity and lithology. By comparing the $BSiO_2$ and TOC signals to regional (GRIP ice-core) and local (e.g. peat archives) climate data sets, it will be possible to assess if the proxies are related to palaeoclimate at LNC.

Palaeoenvironmental interpretation

Lateglacial climate change is characterised by rapid and abrupt high amplitude events (Johnsen *et al.*, 1992; Dansgaard *et al.*, 1993) compared to Holocene palaeoenvironmental change which, until recently, was assumed to have been relatively stable. However, in recent years numerous records (e.g. glacial, ocean cores, lake deposits, ice-core tree lines and tree rings) have shown that the Holocene has not been stable (e.g. Denton and Karlén, 1973; O' Brien *et al.*, 1995; Denton and Nesjie, 1996; Alley *et al.*, 1997; Bond *et al.*, 1997; Campbell *et al.*, 1998; Wagner *et al.*, 2000). The GRIP ice-core palaeotemperature borehole record suggests Holocene temperatures rose sharply from 11 ka cal BP to a peak around 7 to 4 ka cal BP during the Holocene Climatic Optimum when temperatures were 2.5°C *warmer* than today (Dahl-Jensen *et al.*, 1998). The Optimum was followed by a Neoglacial cooling trend that reached a low around 2 ka (Dahl-Jensen *et al.*, 1998); borehole temperatures indicate gradual cooling of around 2-3°C which occurred after 5 ka cal BP (Dahl-Jensen *et al.*, 1998). The Neoglacial cooling trend was punctuated by two major high amplitude events; the so-called "Medieval Warm Period" (800 - 1400 AD) when temperatures were 1°C warmer than today and the "Little Ice Age" (1500 -1750 AD), a pronounced cooling event of around 0.5 to 0.7 °C (Dahl-Jensen *et al.*, 1998) (Figure 9.3). Speleothem, lake and peat records from Britain (Hughes *et al.*, 2000; McDermott *et al.*, 1999) show that Holocene climate change within the UK has been broadly synchronous with the GRIP ice core record within the limits of dating controls. The $BSiO_2$ and TOC records from LNC appear to correspond with these broad trends in the GRIP ice-core (Dahl-Jensen *et al.*, 1998) (Figure 9.3).

The $BSiO_2$ and TOC begin to increase from around 7.5 ka cal BP. $BSiO_2$ peaks around 6 ka cal BP then gradually declines to a minimum around 1.5 ka cal BP. A marked cooling trend is identified between 3 to 1 ka cal BP. Prior to 7.5 ka cal BP, I infer that basin sedimentation was strongly influenced by marine conditions which may have masked any palaeoclimate trend from 9 to 7.5 ka cal BP. The presence of cooler marine waters may have reduced biogenic production and the high minerogenic input, associated with marine inundation, would have also diluted the $BSiO_2$ signal.

The North Atlantic region experienced a cooling event around 8.2 ka cal BP (Alley *et al.*, 1997; Barber *et al.*, 1999) but the TOC and $BSiO_2$ proxies from LNC do not appear to record this event. This is maybe because the sampling resolution is insufficient to detect such a short-lived palaeoenvironmental occurrence or the marine conditions in the basin masked the event in the $BSiO_2$ and TOC records because LNC was a fully marine inlet around 8.2 ka cal BP. Interestingly, there is a peak in brackish water foraminiferal species just prior to *c.* 8.2 ka cal BP (Lloyd, 2000) and a decrease in C/N ratios (Figure 9.1).

At the boundary between Zone 2 and Zone 3, LNC records a peak (137 to 113 cm) and a trough (105 to 89 cm) in both the $BSiO_2$ and TOC signals which is dated between 0.7 to 0.5 ka cal BP (Lloyd, 2000) (Figure 9.3). The TOC signal roughly corresponds with this trend but the trough in $BSiO_2$ correlates with a sample that contained so little carbon it could not be analysed due to the presence of sand lenses in this part of the core. This part of the record could possibly present the influence of the Medieval Warm Period (*c.* 800 – 1400 AD) and the Little Ice Age (*c.* 1550 – 1800 AD).

While LNC data correlates with the broad North Atlantic climate trend preserved within the GRIP ice-core, the data from LNC shows a high degree of variation (Figure 9.3). During the mid and late Holocene a number of high amplitude oscillations in $BSiO_2$ values occur. Four of the most prominent events occur between 485 cm to 169 cm:

1. Between 385 cm to 353 cm, $BSiO_2$ values record lower values around 1.7% to 1.3%.

2. $BSiO_2$ peaks between 345 cm to 313 cm where values increase to around 2.3% to 2.6%.
3. The third event is seen by a reversal back to low $BSiO_2$ values of around 0.5% between 305 cm to 281cm.
4. The fourth event between 193 cm to 169 cm, $BSiO_2$ values drop to around 0.3%.

A number of peat records which examined bog surface wetness of ombrotrophic bogs (Barber *et al.*, 2003; Ellis and Tallis, 2000; Hughes *et al.*, 2000), lake level data (van Geel *et al.*, 1996; Yu and Harrison, 1995) and $\delta^{13}C_{org}$ data from a varved lake (Lüke *et al.*, 2003) and ocean cores which identify peaks in ice rafted debris (IRD) events (Bond *et al.*, 1997) from around the UK and Europe, have identified a number of "events" which are attributed to climate forcing across Northern Europe. Table 9.1 illustrates these events from various records across Europe. A series of major and minor oscillations can be identified according to Barber *et al.* (2003). For example, two peat bogs (Bolton Fell Moss and Walton Moss) indicated minor wet events around 6.2, 5.42 and 5.25 ka cal BP whereas Lake Holzmaar, Germany records a major change in $\delta^{13}C_{org}$ at 5500 varve years BP (Table 9.1), while there is an IRD event at 5.9 ka cal BP (Bond *et al.*, 1997). These minor events could possibly be correlated with minor variations in the $BSiO_2$ record (Figure 9.3). However, both Barber *et al.* (2003) and Hughes *et al.* (2000) argue that between 4.0 to 1.0 ka cal BP, climate across Britain became wetter; the most prominent events occurred at 4.4, 2.7 and 1.7/1.5 ka cal BP. The 2.7 ka cal BP event is widely recorded across Europe (van Geel *et al.*, 1996; Lüke *et al.*, 2003). There are also three prominent IRD events at 4.2, 2.8 and 1.4 ka cal BP (Bond *et al.*, 1997) which correlate with the terrestrial records. The two British peat bogs, Bolton Fell Moss and Walton Moss, also record a dry event that began around 3.9 ka cal BP. These four events broadly correlate with the dating for the mid point of the peak and troughs identified between 485 cm to 169 cm (Figure 9.3 – marked by arrows).

The trough in values correlates with the three main wet events during the mid Holocene (Figure 9.3). This implies that the wetter and cooler climate could have either caused slope wash to increase, causing the $BSiO_2$ to become diluted by increased minerogenic input and / or reduced aquatic productivity due to lower air, compared to warmer and drier climates. These four short-term variations in the $BSiO_2$ record do not always correlate exactly with a similar trend in TOC. One possible reason is because TOC is a measure of both aquatic and catchment productivity, while $BSiO_2$, by definition, is an indicator of solely aquatic productivity (Colney, 1998). Therefore, changes in sediment source may mask TOC signal to palaeoclimate and possibly catchment vegetation takes longer to react to a short-term change in environment. However, the link with these climate events are tentative because these peaks and troughs in the $BSiO_2$ records could present changes in the preservation of $BSiO_2$. Changes in the pH of a lake can effect the preservation of diatoms; an increase in alkalinity can increase diatom dissolution (Flower, 1993). In order to establish if these "events" seen in the LNC record are real and not a product of silica dissolution, a $BSiO_2$ record from a near-by freshwater sequence needs to be analysed to test if the results from the mid Holocene section of LNC can be replicated.

These preliminary results are encouraging. However, comparisons between palaeoclimate records must be undertaken with a degree of caution as the age/depth model has been created with only 4 AMS ^{14}C dates. Four dates are insufficient to construct a high precision geochronology, even when the regression analysis has shown the degree of scatter is very low ($r^2 = 0.99$). Most terrestrial peat or limnic records typically have 10 or more ^{14}C dates and possibly contain a tephra horizon that provides the basis for time-stratigraphic correlations over a sequence of 4 to 5 m (e.g. Mayle *et al.*, 1999; Barber *et al.*, 2003). Despite the inherent errors of the age model created for the new core, similarities in the timing between major climate trends in the GRIP ice-core can be identified, even though environmental factors associated with changes in salinity would have existed. The broad degree of synchronicity of the LNC record with the archives from across the North Atlantic strongly suggest that the $BSiO_2$ and TOC records from LNC is prominently a function of palaeoclimate after 7.5 ka cal BP. Overall, the data suggests that LNC experienced climate amelioration from 7.5 ka cal BP and temperatures peaked around 6.5 ka cal BP. This was followed by Neoglacial cooling that appears to have been particularly severe between around 3 to 1.5 ka cal BP indicated by the repeated lows in $BSiO_2$. This interpretation corresponds well with numerous palaeoclimate reconstructions of the North Atlantic region during the Holocene (e.g. Dahl-Jensen *et al.,* 1998; Kaplan *et al.,* 2002; Hughes *et al.,* 2000). The LNC record may also contain possible evidence for the MWP and the LIA, however, this is a tentative link especially as the MWP is only identified by a peak in one sample. The $BSiO_2$ signal may even correlate with more subtle changes in climate identified in the mid to late Holocene (Table 9.1). However, all correlations, especially during the mid Holocene (i.e. the short term climate events), are dependent on the quality of the age control. In order to confirm this interpretation from LNC, a $BSiO_2$ and TOC record from a nearby freshwater lake would need to be compared.

9.3.2 Upper Loch Nan Eala

Palaeoenvironmental interpretation

The $BSiO_2$ and TOC values follow the general trend of the diatom palaeosalinity record (Shennan *et al.,* 1994). This suggests that $BSiO_2$ and TOC records from ULNE are controlled predominantly by the salinity regime of the basin. Alternatively, the switch from low to higher $BSiO_2$ concentrations across Zones 1 to 2 could be interpreted as the climatic amelioration of the onset of the Holocene Interglacial at *ca.* 11 400 cal BP where there was an abrupt temperature rise of 9°C (Walker *et al.,* 2003). As $BSiO_2$ values >10% are not maintained through the early to Mid Holocene section of the core but return to similar values (<10%) that characterise the Lateglacial marine Zone 1, this suggests the biogenic record is dwarfed by the environmental influences associated with RSL change. The return to $BSiO_2$ values of <10% correlates exactly with the transition to marine Zone 4. This further suggests that palaeosalinity had the largest influence on the $BSiO_2$ and TOC records from ULNE compared to palaeoclimate variables. The low $BSiO_2$ values in the marine sections of the core suggest that there is a high minerogenic input causing dilution of the biogenic signal. The low $BSiO_2$ values which correlate with the peaks in TOC records are due to a change in lithology. For example, the upper section of Zone 7 is composed of peat because the basin has infilled, so it is no longer a lacustrine environment and hence the drop in $BSiO_2$ due to a reduction in diatom productivity in peat environments. There is not a peak in $BSiO_2$ values in Zone 5 because the zone was insufficiently sampled; for example the two levels 230 and 224 cm which form the peak in TOC and C/N ratios were not sampled.

The $BSiO_2$ from ULNE correlates with the palaeosalinity record. This contrasts the record from LNC which shows no direct correlation between the two proxies. This contrast may reflect the different nature of the isolation sequence recorded in each basin. The diatom flora (Shennan *et al.,* 1994) shows that ULNE experienced a number of rapid high-amplitude swings in the salinity regime. The majority of the sediment in the basin is marine or brackish/marine in nature (Zones 1,3,4 and 6). By comparison, LNC experienced a very gradual change in salinity over several millennia, even though there was a significant change in overall environmental regime from the base to the top of the sequence. In LNC case, the majority of the sediment composition is brackish (Lloyd, 2000). The overall greater organic content in LNC appears to preserve a biogenic silica record that correlates to the known palaeoclimate record. This suggests that where isolation sequences comprise highly organic deposits they may indeed provide reliable biogenic silica records of palaeoclimate. In contrast, where the biogenic content is low and the minerganic content high, such as in ULNE (Zones 1,3,4 and 6), the biogenic silica / climate link appears to break down. This implies that the organic content of the sediments is an important control on the potential palaeoclimate signal of the sediment record. Although only two basins have been studied thus far, it would appear that sequences that contain abundant organic material have the greatest potential for palaeoclimate reconstruction using the biogenic silica method.

9.4 Conclusion

1. The $BSiO_2$ and TOC records from LNC show a high degree of correspondence with the GRIP palaeotemperature record. This indicates that the $BSiO_2$ and TOC signals reflect the major hemispheric temperature trends during the Holocene. It is also possible that $BSiO_2$ is a sensitive indicator of short term climate oscillations ("wet/cold" and warm/dry" climatic events) that occurred during the mid to late Holocene. However, this needs to be tested by comparing a $BSiO_2$ and TOC record from a neighbouring freshwater loch.
2. The $BSiO_2$ and TOC signals from ULNE are predominantly controlled by the salinity regime of the basin and the effects of changes in the proportion of minerogenic inputs associated with the changes in salinity. Therefore, the $BSiO_2$ and TOC records from ULNE cannot be used to reconstruct trends in palaeoclimate since the Lateglacial.
3. Overall, the preliminary results from LNC are promising and indicate that palaeoenvironmental records, other than salinity, can be reconstructed from isolation basin sequences. This implies that organic rich isolation basin sequences may provide valuable archives of palaeoclimate and palaeosalinity change. As such, these basins offer the potential to be valuable links between the terrestrial and marine records of palaeoenvironmental change. This implies that organic rich isolation basin sequences may provide valuable archives of palaeoclimate and palaeosalinity change. As such, these basins offer the potential to be

valuable links between the terrestrial and marine records of palaeoenvironmental change. However, only two isolation basin records have been examined and each shows a marked difference in the types of signal. This indicates that further research is required to test if certain types of isolations basin sediments are more or less suitable for palaeosalinity and palaeoclimate reconstruction than others.

4. $BSiO_2$ can be used as an additional proxy to support establish palaeosalinity indicators from sequences which experienced rapid isolation as a result of RSL change.

Chapter 10

Assessment of palaeosalinity proxies

10.1 Introduction

The primary aim of this thesis is to find alternative methods of reconstructing salinity geochemically. The pilot study demonstrated that $\delta^{13}C_{org}$ combined with C/N ratios and $^{87}Sr/^{86}Sr$ isotopic methods were potentially suitable as palaeosalinity proxies. Unfortunately, $^{87}Sr/^{86}Sr$ could not be extended to a more detailed study because insufficient foraminiferal material existed within sediment sequences from the Arisaig field area. The preliminary results presented in Chapter 5, however, suggest that this proxy has the potential to make quantitative reconstructions of palaeosalinity within isolation basin sediments for the first time. Chapters 6 to 8, presented the results of as more detailed investigations of the following proxies; $\delta^{13}C_{org}$ and C/N ratios, $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ and $\delta^{18}O_{diatom}$. Chapter 9 illustrated the use of $BSiO_2$ and TOC to reconstruct palaeoclimate trends from isolation basins sediments. Chapter 9 also showed that $BSiO_2$ variations can follow palaeosalinity trends. This chapter aims to compare and assess $\delta^{13}C_{org}$, C/N ratios, TOC, $\delta^{18}O_{foram}$, $\delta^{13}C_{foram}$, $\delta^{18}O_{diatom}$ and $BSiO_2$ as indicators of salinity. This will be achieved by comparing and evaluating these different methods of palaeosalinity reconstructions against one another using field sites that had multiple isotopic and geochemical analyses carried out on them, such as Upper Loch nan Eala (ULNE), Arisaig and Loch nan Corr, Kintail (LNC) (Figure 3.2 and 3.21).

10.2 Comparison of salinity proxies from the sediment cores ULNE and LNC

A synthesis of all proxies applied to ULNE and LNC is presented in Figures 10.1 and 10.2. ULNE and LNC are ideal for comparing the suitability of individual proxies because each proxy was applied to both sites. In addition, ULNE and LNC contain different types of sequence. As discussed in Chapter 3, ULNE experienced rapid salinity changes across each isolation contact compared to LNC. By examining the two different types of isolation sequence, it can be established whether particular proxies or combination of proxies are better at palaeosalinity reconstruction on particular types of sequences than others.

Sediment core ULNE

The sediment core was divided into seven zones based upon the diatom salinity reconstruction (Shennan *et al.*, 1994) (Figure 10.1). It can be clearly seen in all 7 zones that variations in $\delta^{13}C_{org}$ and C/N ratios correspond with the diatom reconstruction (Figure 10.1).

The data from $\delta^{18}O_{diatom}$ do not correspond with diatom reconstruction. For example in Zones 1 and 4 the diatoms indicate marine conditions. However, the $\delta^{18}O_{diatom}$ data suggests freshwater conditions (Figure 10.1). In Zone 2 the diatoms suggest freshwater conditions existed, but the $\delta^{18}O_{diatom}$ data indicates the environment was marine. In Zones 3 and 7 the $\delta^{18}O_{diatom}$ data agrees with the diatom reconstruction. Despite the $\delta^{18}O_{diatom}$ data in Zones 3 and 7 corresponding with the diatom salinity reconstruction the overall trend in the $\delta^{18}O_{diatom}$ data suggest that $\delta^{18}O_{diatom}$ from ULNE is an unreliable indicator of palaeosalinity. As discussed in Chapter 8, one likely explanation for these results was the use of an inadequate cleaning technique.

The trends in the TOC and $BSiO_2$ data correlate indirectly with the diatom summary. Low TOC and $BSiO_2$ values correlate with the three marine / high minerogenic sections of the core, Zones 1, 4 and 5 (Figure 10.1). In Zone 3 the brackish section of the core, intermediate values are recorded for both proxies. High TOC and $BSiO_2$ values correspond with freshwater zones, such as Zones 2 and 7, however, when the basin becomes infilled at the top of Zone 7 the $BSiO_2$ values decline reflecting the end of aquatic conditions (Figure 10.1).

The data from ULNE suggests the $\delta^{13}C_{org}$ and C/N ratios can reconstruct salinity. TOC and $BSiO_2$ correspond with salinity indirectly. These proxies are influenced by the sharp lithological changes in the sediment.

Sediment core LNC

The sediment core has been divided up into four zones, based upon the foraminiferal reconstruction (Lloyd, 2000) (Figure 10.2). In all four zones the variations in $\delta^{13}C_{org}$ and C/N ratios correspond with the foraminiferal reconstruction.

In Zones 1 to 3 $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ were analysed. The $\delta^{18}O_{foram}$ values remained stable across Zones 1 and 2, even though the foraminiferal reconstruction and $\delta^{13}C_{org}$ and C/N ratios indicate the environment was becoming less saline (Figure 10.2). In Zone 3 only one sample was analysed for $\delta^{18}O_{foram}$, this sample records a lower value, indicating reduced salinity. The $\delta^{13}C_{foram}$ data show a shift from high to lower values in the middle of Zone 2. This sharp shift to lower $\delta^{13}C_{foram}$ values suggests a rapid decline in the marine influence, though the foraminifera data implies the change was gradual. Overall neither the $\delta^{18}O_{foram}$ or $\delta^{13}C_{foram}$ profiles are related to salinity and do not help to characterise the marine and brackish phases of LNC (Figure 10.2).

If TOC and $BSiO_2$ were related to salinity the proxies would be expected to increase across Zone 3 and peak in Zone 4 due to the reduction in the minerogenic input associated with the gradual withdrawal of marine conditions from the basin across Zones 3 and 4. In addition to isolation the basin would have also become progressively shallower and probably warmer, which would help to increase aquatic productivity. The reverse trend is TOC and $BSiO_2$ is observed in Figure 10.2. As discussed in Chapter 9, TOC and $BSiO_2$ in LNC appear to be related to Holocene palaeoclimatic influences.

In summary, the data from ULNE and LNC suggests the only proxies that reliably reconstruct salinity are $\delta^{13}C_{org}$ and C/N ratios.

10.3 Discussion of individual combination of palaeosalinity proxies

Carbon isotope, C/N ratios and TOC

At both ULNE and LNC the $\delta^{13}C_{org}$ and C/N ratios follow the general trend in the biological salinity reconstruction (Figure 10.1, 10.2). These results show that the $\delta^{13}C_{org}$ and C/N ratios can reconstruct salinity from basins which experience both rapid and slow changes in salinity. This is confirmed by the results from other fossil basins, such as Main Loch nan Eala and Rumach VI (see Chapter 6, Figures 6.4, 6.6). Within a particular site it is possible to detect subtle changes in salinity, for example, between brackish and fully marine conditions. This is demonstrated by the difference in $\delta^{13}C_{org}$ values between Zone 3 and Zone 4 from ULNE (Figure 10.1) and the gradual change in $\delta^{13}C_{org}$ values up-core in LNC (Figure 10.2). Also, the technique is capable of detecting rapid short-lived changes in salinity, for example, the rapid short lived freshwater phases (Zone 5) transition interrupting the Holocene marine phases (Zone 4 and 6) in ULNE (Figure 10.1).

The combination of $\delta^{13}C_{org}$ and C/N ratios on extended transitional isolation contacts such as LNC and Rumach VI will successfully reconstruct end-member values between marine and freshwater phases (Figure 10.2 and 6.6b). However, when $\delta^{13}C_{org}$ and C/N ratios are combined with TOC and the established biological salinity indicators (e.g. diatoms and foraminifera) a more compete picture of basin hydrological changes during an isolation events can be gained. At the top of Zone 3 in LNC just before the final isolation of LNC (Zone 3), $\delta^{13}C_{org}$ values increase suggesting a reversal back to more marine conditions, though the foraminiferal data in this instance proves this is not the case (Figure 10.2). The peak in $\delta^{13}C_{org}$ correlates with rising TOC values, which suggests the productivity of the basin is increasing rapidly (due to a reduction in marine inundation). This caused the TDIC pool to become depleted in ^{12}C. This situation leads to phytoplankton and aquatic plants reducing their discrimination against ^{13}C (Herczeg and Fairbanks, 1987; Hollander and McKenzie, 1991). A similar explanation could be used to interpret the $\delta^{13}C_{org}$ trend from the Holocene section of Rumach VI (Figure 6.6b). The foraminifera data suggests a gradual reduction in salinity across the brackish section of the core (Zone 3b, Figure 6.6b) while the $\delta^{13}C_{org}$ values remain relatively stable. However, the TOC gradually increases through out Zone 3b suggesting a gradual change in basin productivity. By combining the $\delta^{13}C_{org}$ with the TOC data, a more accurate picture of palaeoenvironmental change can be gained. This thesis has shown by combing the use of established biological indicators with $\delta^{13}C_{org}$ values, C/N ratios and TOC data a more detailed picture of changes in salinity and hydrological changes that occur during an isolation event.

By using $\delta^{13}C_{org}$ and C/N ratios in tandem, for the first time, information about the source of organic matter in isolation basins can be obtained. For example, determining the relative proportion of marine aquatics versus terrestrial land plants over time. However, because $\delta^{13}C_{org}$ and C/N ratios are derived from measurements on bulk sediment, they mask the individual components that make up the organic matter. Interpretations can only establish the *dominant* source of organic matter. If detailed information about sediment sources is required, compound-specific isotope analyses (CSIA) can be used to confirm the trend of bulk analyses (e.g. Hayes *et al.*, 1990; Jasper and Hayes, 1990). However, CSIA is limited by our poor understanding of the processes affecting the exact distributions of the isotopic composition of individual compounds in organic matter. As a result, interpretation from CSIA can be problematic (Popp *et al.*, 1997).

A number of isolation basins that have sediments older than 12.4 ka cal BP, (e.g. Torr a' Bheithe, Loch Torr a' Bheithe and Loch a' Mhuilinn) do not show the same relationship with $\delta^{13}C_{org}$, C/N ratio and palaeosalinity, (see Chapter 6, Figures 6.12, 6.14 and 6.16 for results). Freshwater $\delta^{13}C_{org}$ measurements are similar to the $\delta^{13}C_{org}$ values for marine sediment. The results are similar to numerous lake sediment records of Lateglacial age across Europe (e.g. Turney, 1999; Nuñez *et al.*, 2002). The palaeoenvironmental influence of the Lateglacial Interstadial, such as poor soil development due to repeated short-term climate deteriorations and reduced atmospheric CO_2 levels, probably caused freshwater aquatics and land plants from Arisaig to record isotopically higher $\delta^{13}C_{org}$ values than Holocene organic material. Therefore, any potential salinity signal within these basins of Lateglacial age cannot be unambiguously identified because the palaeoclimate of the Lateglacial had a significant influence on $\delta^{13}C_{org}$.

Total organic carbon (TOC)

TOC has been applied to all field sites in this thesis and has proved useful in identifying the range of palaeoenvironmental processes which support the interpretation of palaeosalinity or palaeoclimate proxies. In Figure 10.1 the TOC signal can be used to support the palaeosalinity reconstruction made for ULNE. The TOC record from ULNE follows the general palaeosalinity of the biological reconstruction: TOC is low during marine phases and higher in freshwater sections of the core. The generally low TOC values indicate high minerogenic input during marine inundation of the basin causing the TOC to become diluted. The reverse occurs during the freshwater phases (Figure 10.1). Similar results are seen in other rapidly isolated sequences such as MLNE, the Lateglacial section of Rumach VI, LAM, LTB and TB (see Figures 6.15b, 6.12, 6.14, 6.16). The similarity between the TOC trend and palaeosalinity is striking, particularly in the Lateglacial basins TB, LTB and LAM. TOC is the only geochemical proxy that follows the biological palaeosalinity trends in the Lateglacial isolation sequences. The results from rapidly isolated sequences suggest that TOC can aid palaeosalinity reconstructions. However, this proxy is not an alternative palaeosalinity indicator because the trends in TOC in rapidly isolated sequences are linked to changes in lithology not salinity. For example a basin may record a change in lithology from a minerogenic to an organic limus, but this may not be associated with isolation. Numerous freshwater Lateglacial aged sediments have record such a stratigraphy for example Upper Alt Dail Dubh-Asaid, Arisaig (Figure 6.10). The change in lithology is a reflection of degalaciation of a catchment or the transition to a period of climate amelioration with a corresponding increase in catchment and basin productivity, leading to a transition from minerogenic to organic sedimentation. In these freshwater sequences TOC is a reflection of palaeoclimate. The influences of palaeoclimate can be seen on the TOC record from LNC (Figure 10.2). The TOC data in the brackish section of the core, reflects palaeoproductivity of the lake and the catchment response to palaeoclimate warming during the Holocene. Therefore, TOC is not an alternative method to reconstructing palaeosalinity but can be used to support other geochemical and biological palaeosalinity indicators on Holocene and Lateglacial aged sediments.

Based upon the findings in this thesis, it is recommended that TOC should routinely be applied to isolation basin sequences for RSL reconstructions. TOC is not an alternative indicator of salinity but, when used together with $\delta^{13}C_{org}$, C/N ratios and biological indicators, it provides a more detailed picture of all the environmental variables that contribute to palaeoenvironmental change within isolation basins during isolation or connection events.

Oxygen and carbon analysis of foraminifera

These two proxies were only applied to LNC in this thesis because this was the only field site where abundant foraminifera existed. The results from LNC show that $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ do not follow the trends in the biological salinity reconstruction. In Chapter 7, it was suggested that $\delta^{18}O_{foram}$ is possibly insensitive to small changes in salinity that occur when isolation basins experience isolation. Also, it appears that $\delta^{13}C_{foram}$ values are more influenced by microhabitat effects rather than by salinity. This is seen when $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ data is compared with $\delta^{13}C_{org}$ and C/N ratios from LNC (Figure 10.2). $\delta^{13}C_{org}$ and C/N ratios follow the general trend in salinity identified by the foraminiferal reconstruction as $\delta^{13}C_{org}$ values gradually decrease up core reflecting the gradual decrease in salinity through time. The $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ results are surprising given the relative successes of $\delta^{18}O$ and $\delta^{13}C$ from mollusc shells in estuarine environments (e.g. Ingram *et al.*, 1996 – San Francisco Bay), which show a linear relationship with salinity. The same relationship with $\delta^{18}O_{foram}$ and salinity is seen in shallow seas (e.g. Dix *et al.*, 1999) and also in the results of Lloyd and Evans (2002) from the Holocene sediment of the isolation basin Rumach VI in Arisaig. The success of the other marginal marine studies could be attributed to environments experiencing a greater salinity gradient through time and space, especially in estuarine systems where the through-flow of freshwater is greater. However, some studies from non-estuarine environments have had little success with the two proxies from ostracod shells. For example, Mazzini *et al.* (1999) applied the two proxies to Holocene coastal lagoon sediments near the Albegena River, Tuscany. It was found that $\delta^{18}O$ did not relate to salinity particularly during brackish phases of the lagoon due to complex mixing of water sources, coupled with evaporative effects in the lagoon. However, it was found that $\delta^{13}C$ could be broadly correlated with salinity and it was interpreted as a productivity linked signal to freshwater inputs (Mazzini *et al.*, 1999). It has also been found that $\delta^{18}O_w$ from Florida Bay does not correlate with salinity due to a complex mix of water sources and evaporation effects (Swart *et al.*, 1989). These studies highlight the fact that in marginal marine environments, a series of complex processes can easily overprint a potential palaeosalinity signal produced by conservative mixing of two end-member sources of fresh and marine waters.

The results from this study highlight that further work needs to be conducted on $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ from contemporary and fossil isolation basins before they can be considered a reliable indicator of palaeosalinity. Further research will determine if the results from LNC are only site specific or common to many other fossil isolation basin sequences. Also, by examining the contemporary environment, a clearer understanding of the environmental variables controlling $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ signals will be gained. Even if $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ were found to be sensitive to small changes in salinity, the proxy is limited to marine and brackish sections of the core that contain calcareous foraminifera, unlike $\delta^{13}C_{org}$ and C/N ratios. The results from LNC also highlight the difficulties of obtaining a monospecific calcareous foraminiferal sequence for analysis. There is a gap (between 673 and 633 cm, Figure 10.2) in analysis of LNC because *Haynesina germanica* was absent in a section of the core. Therefore, any palaeoenvironmental reconstruction is restricted by preservation of microfossil abundance, which is one of the common problems of existing biological palaeosalinity indicators. Despite previous research from other marginal marine environments, the results of this thesis suggest, $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ are not reliable indicators of palaeosalinity within isolation basin sediments. Therefore, $^{18}O_{foram}$ and $\delta^{13}C_{foram}$ cannot be used as alternative palaeosalinity indicators within isolation basins.

Oxygen isotope analysis of diatoms

As discussed in Chapter 8, no meaningful trend was established from the $\delta^{18}O_{diatom}$ data of ULNE. The full potential of this proxy has not been demonstrated. A range of possible explanations were discussed in Chapter 8. A significant problem was the cleaning technique, which was inadequate to produce samples suitable for analysis. Since analysing ULNE for $\delta^{18}O_{diatom}$, significant advances in the cleaning technique have been made (e.g. Morley *et* *al.*, 2004) and $\delta^{18}O_{diatom}$ is now becoming a more widely-used method for environmental reconstruction in marine and lake sediments that have poor carbonate preservation (e.g. Leng *et al.*, 2001; Hu and Shemesh, 2003; Jones *et al.*, 2004; Rosqvist *et al.*, 2004). The proxy should be re-tested as a palaeosalinity indicator, using the new cleaning procedure. This will not only advance the range of proxies used in sea level research but also broaden the range of environments to which the proxy is applied. $\delta^{18}O_{diatom}$ analyses should be conducted on isolation basin sediments which experienced both rapid and slow changes in salinity in order to establish if $\delta^{18}O_{diatom}$ is sensitive enough to detect small changes in salinity (i.e. <6 psu). Also, $\delta^{18}O_{diatom}$ should be tested upon sediment of Lateglacial Insterstadial age to see if factors such as temperature mask the palaeosalinity signal, which has been shown to clearly affect the $\delta^{13}C_{org}$ as a palaeosalinity indicator during this time.

Biogenic silica

Biogenic silica concentrations were analysed from ULNE and LNC as a palaeoclimate indicator (Figures 10.1 and 10.2). As described in Chapter 9, $BSiO_2$ appeared to follow the general salinity trends in ULNE while in LNC $BSiO_2$ is influenced by palaeoclimate. The reason for the correlation with salinity in ULNE is probably linked to changes in minerogenic input associated with changes in marine inundation, similar to the influence on TOC values from rapidly isolated sequences. The proxy $BSiO_2$ is not a palaeosalinity indicator because it is controlled by changes in minerogenic input and basin productivity. However, on rapidly isolated sequences $BSiO_2$ could be used to support other biological or isotopic palaeosalinity indicators.

10.4 Summary and evaluation of methods

- $\delta^{13}C_{org}$ and C/N ratios appear to be the best alternative geochemical indicator for reconstructing salinity on Holocene aged sediments. The method is not reliant on microfossil preservation and can reconstruct all stages of an isolation or connection event and indicate the source of organic matter to the basin. No other isotopic or biological salinity proxy can be used to provide this level of palaeoenvironmental information.

- TOC concentration should be used to support $\delta^{13}C_{org}$ and C/N ratios and other biological salinity on all types of isolation basin sediment, while $BSiO_2$ will provide additional support for palaeosalinity change upon rapidly isolated sequences.
- $^{87}Sr/^{86}Sr$ could be used for making quantitative reconstructions of palaeosalinity within isolation basin sediments. However, this is dependent on suitable geological setting and abundant carbonate material preserved within the sediment.
- $\delta^{18}O_{diatom}$ should be re-tested as a palaeosalinity indicator using the improved sample preparation technique. This isotope method has the potential to be an alternative palaeosalinity indicator which could be used in combination with $\delta^{13}C_{org}$ and C/N ratios and biological methods.
- Based upon the results from this thesis, $^{18}O_{foram}$ and $\delta^{13}C_{foram}$ should not be used as palaeosalinity indicators from isolation basin sediments.
- Overall, for high-resolution reconstruction of RSL change, multiple geochemical and biological indicators should be applied to isolation basin sediments, in particular, $\delta^{13}C_{org}$, C/N ratios, TOC and biological indicators. This will identify more of the processes that have participated in the palaeoenvironmental change within isolation basins associated with a RSL rise or fall.

Chapter 11

Conclusions and application of research

11.1 Introduction

This chapter summarises the conclusion of the research findings of this thesis, in relation to the original thesis aims and outlines recommendations for the application of this research. The primary aim of this thesis was to investigate possible geochemical means of reconstructing palaeosalinity in order to find alternative methods of reconstructing RSL from isolation basin sediments. A secondary aim was to investigate the usefulness of isolation basins as records of palaeoclimate change by using the proxies, biogenic silica ($BSiO_2$) and total organic carbon (TOC). A further aim was to improve the existing geochronological controls of isolation basin sequences by attempting to identify tephra layers within isolation basins sediments.

11.2 Research findings

Aim 1: Find an alternative method to reconstruct salinity

In total, five combinations of proxies were assessed as alternative palaeosalinity indicators. In Chapter 10 a detailed assessment was made of the different combination of proxies for palaeosalinity. Table 11.1 provides a summary of the applicability of each combination of proxies for palaeosalinity reconstruction within isolation basins.

Table 11.1: Summary of palaeosalinity proxies

Proxy	Assessment of the use palaeosalinity proxy
$\delta^{13}C_{org}$ and C/N ratios	Identifies palaeosalinity trends within temperate aged sediments. Best when combined with TOC. The proxy is also capable of detecting hydrological changes within basins that have extended transitional isolation contacts. A suitable geochemical proxy for temperate sediments devoid of microfossils.
$\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$	Based on the data from one field site the use of $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ on the species *Haynesina germanica* appear to be an unreliable indicator of salinity.
$\delta^{18}O_{diatom}$	The results in this thesis did not successfully reconstruct palaeosalinity. However, the proxy should be retested using the new cleaning technique of Morley *et al.* (2004).
$^{87}Sr/^{86}Sr$	The proxy is capable of making quantitative measurements of palaeosalinity. However, the proxy is reliant on sufficient carbonate material being present in the sediment.
Major, trace and rare earth elements	Not a suitable proxy for palaeosalinity reconstruction within isolation basin sediments

For best results multi-proxy studies are recommend which combine geochemical ($\delta^{13}C_{org}$, C/N ratios and TOC) and established palaeosalinity proxies (e.g. diatoms or foraminifera). This will create high-resolution palaeosalinity reconstructions from isolation basin sediments.

Aim 2: Palaeoclimate

It was found that $BSiO_2$ and TOC concentrations from organic rich isolation basins isolation basin sediments can be correlated with other palaeoenvironmental archives around the North Atlantic region. As such, these basins offer the potential to be valuable links between the terrestrial and marine records of palaeoenvironmental change.

Aim 3: Tephrochronology

This thesis set out to find the Vedde Ash tephra, because it had been found in high abundance around Northwest Scotland. In total, five sites were examined and no micro tephra layers were found in either freshwater or marine phases of isolation basin sediment from Arisaig. The likely cause is either the Vedde was not deposited in the area, catchment dynamics or the effects of tidal scouring prevented tephra being deposited in sufficient quantities for accurate identification.

11.3 Applications of research

The use of $\delta^{13}C_{org}$, C/N ratios and TOC should be routinely applied to RSL reconstructions from isolation basin sediments of Holocene age in conjunction with established biological palaeosalinity indicators. A multi proxy approach enables a more complete understanding of the different environmental processes that occur during RSL change within isolation basins.

Isolation basin sediments of Lateglacial age should use a combination of conventional biological indicators, coupled with TOC and possibly $BSiO_2$, as they will possibly give additional information on productivity. A combination of proxies will provide a multiproxy approach to RSL reconstruction of Lateglacial Interstadial sediments.

The application of $\delta^{18}O_{diatom}$ as a palaeosalinity indicator has great potential. Further research is needed to determine the fractional relationship between $\delta^{18}O_{diatom}$ and salinity. Also, it needs to be established whether vital effects will influence palaeoenvironmental interpretations within isolation basins. The proxy also has the potential to detect the influence of meltwater pulses in isolation basin sediments because it is able to trace differences in $\delta^{18}O$ of ambient water masses. The technique will be particularly useful in Arctic environments, where carbonate contents are low but isolation basins are abundant in diatoms. If quantitative reconstructions of palaeosalinity are required, $^{87}Sr/^{86}Sr$ is recommended, combined with other palaeosalinity indicators. However the local geology may restrict the use of the technique.

The ability for palaeoclimate reconstruction from isolation basin sediments should be exploited further. The best results are likely to be obtained from basins that experience slow changes in salinity. The proxy $\delta^{18}O_{diatom}$ may also have potential as a palaeoclimate indicator in slowly isolated sequences, as it has been used as a palaeoclimatic proxy in lake sediments.

While tephra analysis did not work on sediments from Arisaig, the technique should still be tried in other areas because the results from this thesis might be site specific. The proxy is still an ideal method for geochronological correlations in isolation basins because it provides a means of correlating RSL histories with other palaeoenvironmental archives across the North Atlantic accurately and precisely.

11.4 Thesis conclusion

In conclusion, this thesis has contributed to both sea level and isotopic research fields. I have tested a number of alternative isotopic and geochemical methods for palaeosalinity reconstruction for isolation basin sediments. I have also determined which methods are particularly suitable for certain types and ages of isolation basin sediments. In discovering a range of alternative methods this thesis has demonstrated a fuller understanding of the complex changes that isolation basins experience during isolation or connection events. Also, the benefits of multi-proxy palaeosalinity studies have been shown. In addition, by testing a range of isotope methods I have highlighted the different limitations of isotope analysis that should be taken into account when applying them to sea level studies. This thesis has also found isolation basins can contain high-resolution palaeoclimatic information which could be applied to studies of land-ocean interactions.

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Foraminifera

1. Between 4 and 6 foraminifera were placed in a clean Savillex becker containing 2 mls of millQ water and 1 ml of 10% acetic acid. Samples were left overnight. If samples did not dissolve they were sealed and warmed gently on a hotplate for 15 minutes.
2. Dissolved samples were transferred to a clean and labelled centrifuge tubes and centrifuged at 3500 rpm for 10 minutes.
3. Supernatant liquid was pipetted into clean Savillex beakers and evaporated on the hotblock to dryness.
4. ~1-2 ml 6M HCL was added to convert acetate to chloride and then evaporated
5. The residue was taken up in 1.2 ml of 2.5M HCL and transferred to clean centrifuge tubes.
6. 1 ml was loaded on preconditioned ion exchange column and Sr fraction eluted as before.
7. Columns are washed after use with 50 ml 6M HCL, followed by 50 ml of millQ water. A second 50 ml of 6M HCL was then added. Finally, 20 ml of 2.5M HCL was added to precondition the each column.

Water samples were loaded on single tantalum filaments prepared with 1M phosphoric acid. Foraminifera were loaded on rhenium filaments with a TaF activator. Isotope ratios were measured on a Finnegan 262 mass spectrometer run in multidynamic mode. Measured ratios were corrected for fractionation relative to $^{87}Sr/^{86}Sr$ = 0.1194 and normalised to a value of 0.710248 for the NBS 987 Sr isotope standard. Eight determinations of North Atlantic Seawater yielded a mean value of 0.709175 ± 0.000016 (2sigma).

Sequential leaching and REE

A four stage sequential leach method adapted from Tessier *et al.* (1979).

Stage 1 (exchangeables)

1. Weigh 1 g dry whole sample into Nalogene bottle.
2. Add 20 ml 1Ma NaOAc.
3. Agitate for 1 hour at room temperature.
4. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
5. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.
6. Add 20 ml mQ water and agitate briefly.
7. Centrifuge at max g (circa 4000 rpm) for 30 mins.
8. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.

Stage 2 (carbonates)

1. Add 20 ml 1M NAOAc buffered to pH 5 with acetic acid to residue from Stage 1.
2. Agitate for 5 hours at room temperature.
3. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
4. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.
5. Add 20 ml mQ water and agitate briefly.
6. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
7. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.

Stage 3 (Fe and Mn bound)

1. Add 20 ml of a solution of 0.3M $Na_2S_2O_4$, 0.175M Na-citrate and 0.025M citric acid to residue from stage 2.
2. Agitate for 8 hours at room temperature.
3. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
4. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.
5. Add 20 ml mQ water and agitate briefly.
6. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.

7. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.

Stage 4 (organics)

1. To residue from stage 3 add 7.5 ml 0.02M HNO_3 then 12.5ml 30% H_20_2 (adjusted to pH2 with HNO_3).
2. Leave for 2 hours at 85°C (in oven or on hotplate) with occasional agitation.
3. Add a further 7.5 ml aliquot of H_20_2 (pH2).
4. Leave for 3 hours at 85°C (in oven or on hotplate) with occasional agitation.
5. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
6. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.
7. Add 20 ml mQ water and agitate briefly.
8. Centrifuge at maximum g (circa 4000 rpm) for 30 mins.
9. Decant supernatant to Sterilin flask with 0.1 ml HNO_3.

Appendix II

List of foraminifera and diatoms counts used to correlate the sediments cores: Upper Loch nan Eala (ULNE), Maine Loch nan Eala (MLNE) Rumach VI –Lateglacial core, Loch Torr a' Bhethie (LTB), Torr a' Bheithe (TB) and Loch a' Muilinn (LAM).

Craiglin Lagoon Diatom count from sample Station 1

Polyhalobous	
Cocconies scutellum	18
Paralia sulcata	135
Rhabdonema minutum	15
Rhabdonema musculus	10
Triceratum anteedilurianm	2
Brackish (mesohalobous)	
Navicula digitoradiata	19
Fresh	
Epitherma sorex	2

Upper Loch nan Eala

ULNE – 665 cm

Marine	
Diploneis litoralis	16
Paralia sulcata	12
Pleurosigma	10
Rhabdonema minutum	71

Brackish	
Dipleneis didyma	5
Fresh	
Cocconies placentula	17
Cyctella plitvicensis	1
Epithemia sorex	2
Halophobous	
Cyclotella antiqua	2
Eunotia arcus	2

ULNE 148 cm

Fresh	
Cymbella lunta	7
Epithemia zebtra	5
Fragilaria brevistriata	33
Fragilaria pinnata	55
Gomphonema acuminatum	13
Navicula radiosa	5
Halophobous	
Eunotia arcus	2
Tabellaria flocculosa	80

ULNE 174

Marine	
Paralia sulcata	13
Fresh	
Cymbella tumidula	2
Epithemia zebra	105
Fragilaria brevistriata	7
Fragilaria pinnata	50
Gomphonema acuminatum	5
Navicula radiosa	16
Opephora martyi	
Halophobous	

Eunotia arcus	2
Tabellaria flocculosa	12

ULNE 180 cm

Marine	
Amphora maxicaua	6
Cocconies scutellum	2
Paralia sulcata	34
Navicula hennedyi	4
Brackish	
Rhabdonema musclus	4
Fresh	
Cocconies placentula	24
Fragilaria brevistriata	35
Fragilaria pinnata	88
Navicula radiosa	3

ULNE 487 cm

Marine	
Cocconies scutellum	19
Ciplonies litoralcs	7
Paralia sulcata	82
Rhabdonema minutum	15
Brackish	
Amphora exigua	5
Dipories didyma	10
Fresh	
Cocconies placentula	2
Cyctella radiosa	5
Cymbella aspera	17
Epithermia goeppertiana	1
Epithemia sorex	9
Fragilaria brevistriata	11
Navicula radiosa	8

Halophobous

Cyclotella antiqua	1
Eunotia arcus	23

ULNE 535 cm

Marine

Paralia sulcata	142
Rhabdonema minutum	1

Brackish

Rhopalodia gibba	1

Fresh

Cyctella sp	8
Epithemia sorex	7
Fragilaria brevistriata	11
Gomphonema acuminatum	1

Halophobous

Cyclotella antiqua	3
Eunotia arcus	26

ULNE 543 cm

Fresh

Amphora var capitata	3
Amphora sp.	10
Anomoeoneis sphaerophora sp.	2
Bracheysira brebissonic	5
Cyclotella comta	15
Cyclostephanos dubis	2
Cyclotella meneglenïana	35
Cymbella Helvetica	5
Cyclotella leptocevas	34
Epithemia sorex	17
Epithemia adnata	9
Epithemia goeppertiana	1
Gomphonema acuminatum	3
Navicula radiosa	7

Holophobous

Eunotia arcus	45

ULNE 644 cm

Fresh

Cocconies placentula	74	
Cymbella caespitose	36	
Cymbella var. nonpunctata	10	
Epithemia sorex	16	
Epithemia zebra	4	
Fragilaria construeus	38	
Navicula radiosa	9	
Nitzchia sinuta		3
Stauronies phoenicenterar	1	

Halophobous

Eunotia arcus	4

ULNE 647 cm

Marine

Cocconies scutellum	4
Diploneis litoralcs	1
Paralia sulcata	36
Rhabdonema minutum	17

Brackish

Navicula forcipata	3
Rhopalodia musculus	6

Fresh

Cocconies placentula	72
Epithemia sorex	19
Fragilaria brevistriata	7
Fragilaria construens	7
Fragilaria pinnata	6

Halophobous

Tabellaria flocculosa	4

ULNE 663 cm

Marine

Cocconies scutellum	42
Diploneis litoralcs	7
Paralia sulcata	29
Podosira stelliger	2
Rhabdonema minutum	29
Surrirella comis	1

Brackish

Dipories didyma	4
Navicula diditiradiata	5
Rhopalodia gibba	5
Rhopalodia musculus	7
Rhopalodia rupestis	1

Fresh

Cocconies placentula	18
Epithemia sorex	6
Epithemia var sp.	1
Epithemia zebra	1
Fragilaria brevistriata	5
Fragilaria pinnata	5
Navicula radiosa	3

Holophobous

Cyclotella menegheniana	8
Eunotia arcus	19

Main Loch nan Eala

MLNE 144 cm – *top core sample to show that Holocene freshwater section is missing*

Polyhalobous (Marine)

Paralia sulcata	187
Rhabdonema minutum	5

Mesohalobous (brackish)

Achnanthes brevipes	4
Caloneis frmosa	2

Diploneis didyma	2

MLNE – 360 cm

Marine Polyhalobous

Amphora graeffeana	11
Cocconies scutellum	10
Diploneis litorias	7
Grammatophora oceanica	5
Paralia sulcata	29
Opehora martya	6
Rhabdonema minutum	8

Brackish (mesohalobous)

Amphora exigu	27
Epithemia turgida	4
Navicula digitoraradiata	7
Rhopalodia gibberula	4

Fresh **Oligohalobous)**

Amphora copulata	7
Caloneis sp	2
Cocconeis placentula	2
Cyclotella radisa	2
Epithemia sorex	8
Gomphonema acuminatum	3
Opehora matya	6

Halophobous

Eunotia arcus	11
Tabellonia fenestrata	**1**
Navicula sp.	**9**

MLNE – 362 cm

Marine Polyhalobous

Amphora graeffeana	2
Cocconies scutellum	5
Diploneis litorias	2
Paralia sulcata	2
Opehora martya	13

Brackish (mesohalobous)

Amphora sp	6
Anomoeneis sphaerophora	1
Diploreis elliptica	1
Navicula digitoraradiata	2
Rhopalodia gibba	3

Fresh **Oligohalobous)**

Cocconeis placentula	22
Cyclotella radiosa	9
Epithemia sorex	3
Epithemia zebra	2
Fragilaria brevistrata	47
Fragilaria pinnata	15
Gomphonema acuminatum	5
Navucula begeri	20

Halophobous

Eunotia arcus	11
Tabellonia fenestrata	**27**
Tabellonia floculosa	**4**

MLNE - 364 cm

Oligohalobous (Fresh)

Cocconies placentula	12
Cyctella kützingiana	9
Epithemia sorex	16
Epithemia zebra	3
Fragilaria brevistriata	34
Fragilaria pinnata	18
Fragilaria subcapitata	6
Gomphonema acuminatum	12
Navicula radiosa	18
Nitzschia navicularis	2
Opephora martyi	28

Holophobous

Eunotia arcus	14
Eunotia diodon	3
Tabellaria fenestrata	6

Tabellaria flocculosa	14

MLNE – 394 cm

Oligohalobous	
Amphora	26
Cocconies placentula	26
Epithemia sorex	7
Epithemia zebra	3
Fragilaria brevistriata	64
Fragilaria construns	2
Gomphonema acuminatum	8
Navicula radiosa	9
Navicula laneolata	6
Nitzchea navialovis	1
Pinularia mesolepta	5
Opephora martyi	10

Holophobous	
Cyclotella antique	2
Cyclateela menginla	2
Cyclatella socialis	5
Eunotia arcus	10
Tabellaria floculosa	12
Tabellaria penestrata	13

MNLE 410 cm

Polyhalobous (marine)	
Amphora prottus	1
Cocconies scutellum	2
Diploneis litoralcs	1
Paralia sulcata	15
Pleurosigma aestuarii	2
Rhabdonema minutum	5

Brackish (mesohalobous)	
Amphora exigua	9
Diploreis parma	7
Ropaalodia rupestris	13
Syneda tabalata	11

Navicula digitoradiata	4

Oligohalobous (fresh)

Cocconies placentula	37
Cymbella sp.	28
Epithemia sorex	*15*
Epithemia zebra	16
Epithemia porcelud	*2*
Fragilaria construns	1
Gomphonema acuminatum	11
Navicula contenta	1

Haolophobous

Cyclatella socialis	
Eunotia arcus	*5*

Rumach VI –Lateglacial core

Rumach VI 1039 cm

Fresh (Oligohalobous)

Epithemia sorex	13
Fragilaria brevistriata	27
Fragilaria construens	42
Fragilaria pinnata	80
Gomphonema acuminatum	5
Opephora martyi	2
Cyclatella kutzngiana	1

Halophobous (indifferent)

Eunotia arcus	5
Eunotia jemtlandica	5
Tabellaria flocculosa	1

Rumach VI 1000 cm

Fresh **Oligohalobous**

Cocconies placentula	2
Epithemia sorex	23
Epithemia zebra	2
Fragilaria brevistriata	70
Fragilaria pinnata	61

Gomphonema acuminatum	3
Navicula radiosa	3

Halophobous (indifferent)

Eunotia arcus	8
Eunotia jemtlandica	1

Rumach VI 1045 cm

Polyhalobous (Marine)

Cocconies scutellum	4
Diploneis litoralcs	2
Grammatophora oceanica	2
Paralia sulcata	189
Rhabdonema minutum	2
Surella fastuosa	1

Rumach VI 1051 cm

Marine Polyhalobous

Cocconies scutellum	5
Paralia sulcata	194
Rhabdonema minutum	1

Rumach VI 992 cm v. poor preservation

Marine Polyhalobous

Amphora sp.	3
Anlacodisus	1
Cocconies scutellum	8
Duploneis smithii	2
Grammatophora oceanica	4
Paralia sulcata	38
Rhabdonema minutum	2

Fresh (Oligohalobous)

Epithemia sorex	2
Epithemia goeppertiana	1

Halophobous

Eunotia arcus	1

Rumach VI - 998 cm – poor preservation

Marine Polyhalobous	
Cocconies scutellum	5
Diploneis litorias	2
Grammatophora oceanica	
Paralia sulcata	48
Navicular farcipate	1
Navicular pusilla	1

Brackish (mesohalobous)	
Achnanthes delicatula	1
Achnanthe brevipes	9
Nitzchia pusilla	1

Fresh **Oligohalobous)**	
Epithemia sorex	14
Epithemia zebra	2
Epithemia adnata	
Fragilaria pinnata	14

Holophobous	
Cyclotella antique	2
Eunotia arcus	10

Lateglacial sediment cores

Loch A' Mhuilinn

LAM 751 cm

Polyhalobous (marine)	
Paralia sulcata	188
Rhabdonema minutum	2

Mesohalobous (brackish)	
Achnanthes delicatula	2

Oligohalobous (fresh water species)	
Anomoeonies sphaerophora	1
Epithemia sorex	1
Epithemia zebra	2
Gomphonema acuminatum	1

Halophobous (indifferent)

Cyclotella antiqua	1
Eunotia arcus	1

LAM 749 cm

Mesohalobous (Brackish species)

Rhopalodia parallela	6
Rhopalodia rupestris	14

Oligohalobous (fresh)

Cocconies placentula	3
Cyctella meneglutin	1
Epithemia sorex	51
Epithemia zebra	26
Fragilaria construens	4
Fragilaria brevistriata	7
Fragilaria piñata	16
Gomphonema acuminatum	9
Navicula radiosa	3
Nitzchia sinuta	2
Opephora martyi	34

Holophobous (indifferent)

Cyclotella antiqua	9
Eunotia arcus	11
Tabellaria flocculosa	4

Torr a' Bheithe

TB - 776 cm

Mesohalobous

Rhopalodia gibberula	3

Oligohalobous

Cocconies placentula	2
Epithemia sorex	104
Epithemia zebra	17
Fragilaria construens	18
Fragilaria constricya	6

Gomphonema acuminatum	8
Navicula radiosa	4
Opephora martyi	12

Halophobous

Cyclotella antiqua	24
Tabellaria flocculosa	2

TB - 778 cm

Polyhalobous

Cocconies scutellum	130
Plagiotropis maxima	8
Sururella fastuosa	10

Loch Torr a' Bheithe

LTB – 550 cm

Oligohalobous (fresh)

Cocconies placentula	2
Epithemia sorex	5
Fragilaria brevistriata	22
Fragilaria construens	36
Fragilaria pinnata	26
Opephora martyi	110

Holophobous

Eunotia arcus	2
Tabellaria perestrara	*1*

Loch nan Corr Foraminiferal counts

633 cm	Ammonia beccarii var.	4
	Bulimina marginata	35
	Cibicides lobatulus	1
	Elphidium gerthi	14
	Elphidium macellum	22
	Hangensia	55
	Egg scuff	7

641 cm	Ammonia beccarii var.	5
	Bulimina marginata	2
	Cibicides lobatulus	42
	Elphidium gerthi	21
	Elphidium macellum	73
	Elphidium williamsoni	2
	Hangensia	4
	Egg scuff	10
	Planorbulina meediterrensis	4
657 cm	Ammonia beccarii var.	4
	Bulimina marginata	
	Cibicides lobatulus	35
	Elphidium gerthi	20
	Elphidium macellum	54
	Ephidium margeritaceum	45
	Planorbulina meediterrensis	9
	Sigmoilosi schlumbergen	5
665 cm	Ammonia beccarii var.	3
	Bulimina marginata	
	Cibicides lobatulus	31
	Elphidium gerthi	70
	Elphidium macellum	32
	Ephidium margeritaceum	2
	Planorbulina meediterrensis	18
	Quinqueloculina spp.	19
689 cm	Ammonia beccarii var.	82
	Elphidium macellum	14
	Ephidium margeritaceum	18
	Hangensia	26
	Planorbulina meediterrensis	2
713 cm	Ammonia beccarii var.	50
	Cibicides lobatulus	4
	Elphidium macellum	110
	Elphidium williamsoni	24
	Hangensia	34
	Planorbulina meediterrensis	1
	Diflugia oblonga	1
609 cm	Hangensia	51
	Egg scuff	7
	Bulimina elegantissima	2

569 cm	Hangensia	68
	Elphidium williamsoni	2
131 cm	Miliammina fusca	2
139 cm	Miliammina fusca	7