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Alkenones, alkenoates, and organic matter in coastal environments of NW Scotland: Assessment of potential application for sea level reconstruction

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[1] Reconstruction of late Quaternary sea level history in areas of glacioisostatic uplift often relies on sediment archives from coastal isolation basins, natural coastal rock depressions previously isolated from or connected to the sea at different times. Proxy indicators for marine, brackish, or lacustrine conditions combined with precise dating can constrain the time when the sea crossed the sill threshold and isolated (or connected) the basin. The utility of isolation basins in investigations of sea level change is well known, but investigations have been mostly limited to microfossil proxies, the application of which can be limited by preservation and nonanalog problems. Here we investigate the potential of long-chain alkenones, alkenoates, and bulk organic parameters (TOC, C_{org}/N) for reconstructing past sea level changes in isolation basins in NW Scotland. We analyze organic biomarkers and bulk parameters from both modern basins (at different stages of isolation from the sea) and fossil basins (with sea level histories reconstructed from established proxies). Logit regression analysis was employed to find which of the biomarker metrics or bulk organic measurements could reliably characterize the sediment samples in terms of a marine/ brackish or isolated/lacustrine origin. The results suggested a good efficiency for the alkenone index $\%C_{37:4}$ at predicting the depositional origin of the sediments. This study suggests that alkenones could be used as a novel proxy for sea level change in fossil isolation basins especially when microfossil preservation is poor.

1. Introduction

1.1. Isolation Basins

[2] Coastal isolation basins are natural coastal rock depressions isolated from or connected to the sea by changes in relative sea level (RSL). The utility of isolation basins in investigations of RSL change is demonstrated by research in Scandinavia [*Eronen et al.*, 2001; *Kjemperud*, 1981; *Svendsen and Mangerud*, 1987], Greenland [*Bennike*, 1995; *Long et al.*, 1999], Canada [*Retelle et al.*, 1989], Russia [*Corner et al.*, 1999; *Snyder et al.*, 1997] and Scotland [e.g., *Shennan et al.*, 1993, 2000, 2005]. Isolation basins on the north and west coasts of Scotland yield the longest archives of RSL change in the world (>16 cal kyr to present [*Shennan et al.*, 2000, 2005]). The data obtained from isolation basins are used to test hypotheses in sea level studies derived from morphological work and various isostatic models [e.g., *Shennan et al.*, 1995, 2000, 2005], contributing to scientific understanding of glacial isostatic adjustment and timing and rates of deglaciation since the Last Glacial Maximum [*Peltier*, 1998].

[3] Figure 1 illustrates a conceptual model of the changes in a basin through time during an isolation process caused by a fall in RSL. The final isolation of the basin from the sea [*Kjemperud*, 1986], i.e., the transition from brackish to fresh water environment (from isolation stage 4 to isolation stage 5 in Figure 1), is the key time horizon in RSL change studies. It corresponds to the time when the highest astronomical tide (HAT) falls below the height of the sill (for a summary of tidal cycle terms see EA-1 in Text S1 in the auxiliary material).[1] This may be represented in sediments by a horizon referred to as the isolation contact.

[4] Reconstruction of sea level changes is usually based on lithostratigraphic and biostratigraphic (e.g., microfossil) parameters, although recent work has shown the potential of coupled bulk organic $\delta^{13}C$ and C_{org}/N measurements [*Mackie et al.*, 2005, 2007]. Established microfossil proxies, such as foraminifera or diatoms, are sometimes partially or entirely absent from isolation basin sediments. The allocation of a correct indicative meaning (i.e., the vertical relationship between the local environment in which a sea level indicator accumulated and a contemporaneous reference tide level) is also proxy-dependent. Therefore, multiproxy studies provide a more complete and subtle record of RSL change, leading to greater confidence in conclusions than studies based on single-proxy reconstructions.

[5] This paper assesses the potential application of alkenones and bulk organic parameters as indicators of RSL change in isolation basins. First, we describe the distributions of the lipid compounds and bulk parameters of interest in modern coastal basins, to assess their relationship to the degree of isolation from the sea. Second, we compare the organic parameters with records of established sea level indicators in a number of cores from fossil basins. We are especially interested in determining the potential of long-chain methyl and ethyl alkenones (hereafter alkenones) for RSL work, because measures derived from alkenones have showed potential to identify changes in relative surface salinity conditions [*Bendle et al.*, 2005; *Harada et al.*, 2003; *Rosell-Mele et al.*, 2002; *Rosell-Melé*, 1998; *Seki et al.*, 2005].

1.2. Lipid Biomarkers and Bulk Organic Parameters

1.2.1. Alkenones and Alkenoates in Lacustrine, Coastal, and Brackish Environments

[6] Alkenones are long carbon chain (C_{37} to C_{40}) ketones with 2 to 4 double bonds or unsaturations. Together with the structurally related alkyl alkenoates, they form a suite of compounds that is ubiquitous in ocean sediments (Figure 2). A summary of alkenone (and related alkenoate) measures and other parameters used in this paper is given in Table 1. Alkenones are known to be synthesized by a limited number of unicellular algae of the Haptophyta, which include the coccolithophorids and are often informally called haptophytes [e.g., *Conte et al.*, 1995; *Marlowe et al.*, 1984; *Volkman et al.*, 1980]. Alkenones have been studied extensively in
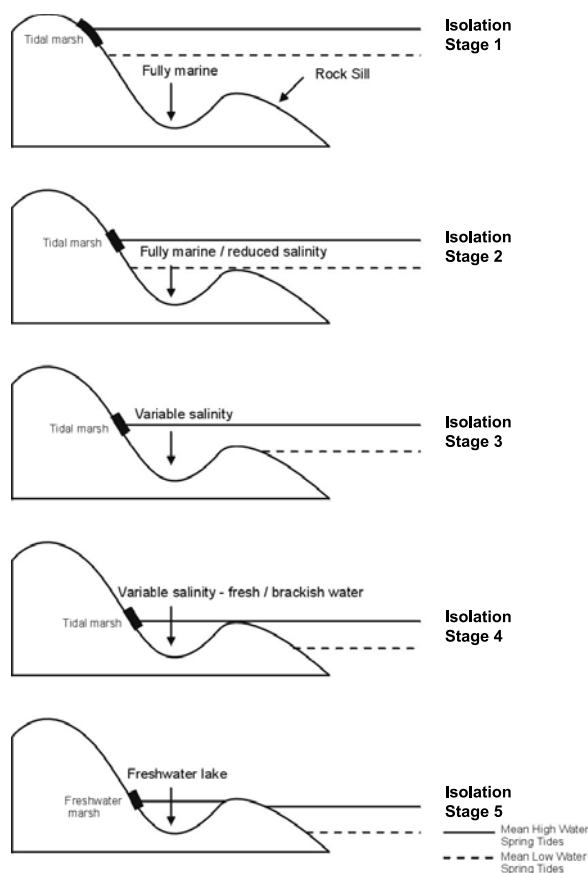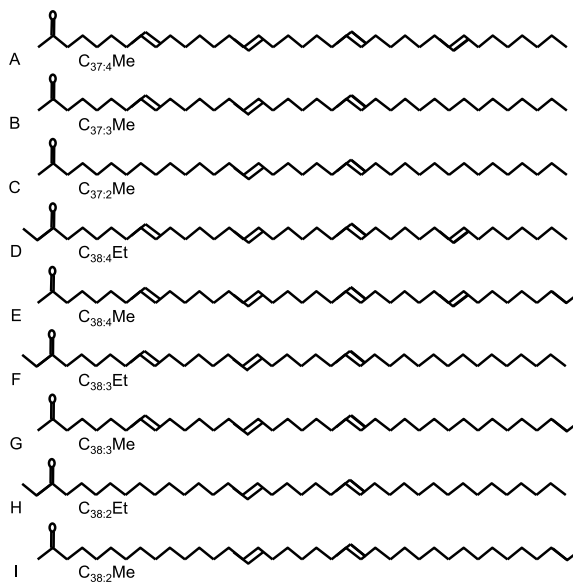
Figure 1. Schematic representation of an isolation basin during a fall in relative sea level (RSL) (adapted from *Shennan et al.* [1996]).
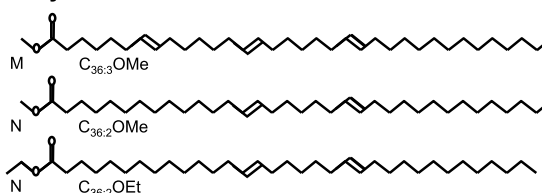

Figure 2. Structures and shorthand notation of long-chain alkenones and alkenoates commonly found in marine and some freshwater environments.

the open ocean, where the temperature-dependent distribution of the $C_{37:2}$ and $C_{37:3}$ alkenones (as expressed in U^K_{37}) has been confirmed by culture, surficial sediment and water column particulate organic matter (POM) studies [e.g., *Conte et al.*, 2006; *Müller et al.*, 1998; *Prahl and Wakeham*, 1987]. After initial work by *Cranwell* [1985] alkenones were rarely reported in lake environments; but recently increasing attention has been given to alkenone distributions and their precursor organisms in lacustrine environments [*Chu et al.*, 2005; *D'Andrea*

and *Huang*, 2005; *D'Andrea et al.*, 2006; *Liu et al.*, 2008; *Sun et al.*, 2007; *Volkman et al.*, 1988; *Zink et al.*, 2001]. However, reports from brackish environments remain rare [e.g., *Conte et al.*, 1994a; *Ficken and Farrimond*, 1995; *Schulz et al.*, 2000]. Lacustrine environments which contain alkenones vary widely in geographical location and environment, including freshwater lakes in the English Lake District, Russia, Germany and China [*Chu et al.*, 2005; *Cranwell*, 1985; *Zink et al.*, 2001] and saline

Table 1. Alkenone Measures Used in This Paper[a]

Measure	Equation	Reference
$U^K_{37'}$	$C_{37:2}Me/(C_{37:2}Me + C_{37:3}Me)$	*Prahl and Wakeham* [1987]
$\%C_{37:4}$	$C_{37:4}Me/(C_{37:2}Me + C_{37:3}Me + C_{37:4}Me) \cdot 100$	*Rosell-Melé et al.* [1998]
$C_{38}Et/Me$	$(C_{38:2}Et + C_{38:3}Et + C_{38:4}Et)/(C_{38:2}Me + C_{38:3}Me + C_{38:4}Me)$	adapted for this paper to include $C_{38:4}Me$ from *Conte et al.* [1998]
$\Sigma C_{37}/\Sigma C_{38}$	$(C_{37:2}Me + C_{37:3}Me + C_{37:4}Me)/$ $(C_{38:2}Et + C_{38:3}Et + C_{38:4}Et + C_{38:2}Me + C_{38:3}Me + C_{38:4}Me)$	*Prahl et al.* [1988]
$\%AA$	$(\Sigma alkyl\ alkenoates/\Sigma alkenones) \cdot 100$	*Sawada et al.* [1996]

[a] See Figure 2 for chemical structures.

lakes in China, Antarctica, Turkey and Greenland [*Chu et al.*, 2005; *D'Andrea and Huang*, 2005; *Li et al.*, 1996; *Sheng et al.*, 1999; *Thiel et al.*, 1997; *Volkman et al.*, 1988].

[7] Only a few previous studies have highlighted the potential of alkenones for investigating environmental change in coastal environments. In a core extracted from Framvaren Fjord (Norway) *Ficken and Farrimond* [1995] found a large increase in the abundance of alkenones in the down-core phase coincident with the intrusion of marine waters to the fjord sediments. Alkenones were also deposited in the sediments during the earlier lacustrine phase, but at a much lower abundance relative to total organic carbon (TOC) [*Ficken*, 1994], and with higher %$C_{37:4}$ (mean 26%). The alkenones in the water column and surface sediments of the brackish marginal Skagerrak and Baltic Seas have distinct characteristics: %$C_{37:4}$ correlates inversely with the salinity gradient (~33 to ~8 psu) and generally decreasing abundances of total C_{37} alkenones, while C_{38}Me compounds are undetectable [*Blanz et al.*, 2005; *Schulz et al.*, 2000]. Elevated %$C_{37:4}$ in sediments associated with the fresher Baltic Sea and the lacustrine phase of the Framvaren fjord sediment core contrast with much lower %$C_{37:4}$ (typically less than 5%) in the global middle- to low-latitude oceans, suggesting that in coastal settings %$C_{37:4}$ has the potential to discriminate between marine, brackish or freshwater environments.

[8] *Schulz et al.* [2000] showed that changes in the ratio of the C_{38}Et to C_{38}Me alkenones helps to distinguish marine *Emiliania huxleyi* source alkenones from alkenones produced either by an unknown source or from a physiologically stressed *E. huxleyi* assemblage in low salinity (<7.7 psu) waters. Other authors suggest that alkenone inputs from the species *E. huxleyi* and *Gephyrocapsa oceanica* can be distinguished by their C_{37}/C_{38} alkenone or alkenoate/alkenone ratios [*Prahl et al.*, 1993; *Rosell-Melé et al.*, 1993; *Sawada et al.*, 1996] or by a plot of U_{38}^KEt against U_{38}^KMe unsaturation ratios [*Conte et al.*, 1998]. Therefore in a study of marginal environments where the alkenone patterns may correspond to changes in biological precursor assemblages or salinity-induced physiological stress, it is important to monitor changes in the full suite of alkenones and alkenoates.

1.2.2. Bulk Organic Parameters: TOC and C_{org}/N

[9] Sedimentary trends in TOC depend on changes in export primary productivity and diagenesis. The latter are influenced by factors such as O_2 content, residence time in the water column and at the sediment/water interface before deposition, molecular reactivity, formation of macromolecular complexes, adsorption to mineral surfaces and bioturbation [e.g., *Killops and Killops*, 2005; *Meyers and Ishiwatari*, 1993a, 1993b].

[10] The natural imprint of organic matter in marginal basin environments includes both autochthonous and allochthonous contributions. The autochthonous input is composed of the material generated within the basin (e.g., products of microalgae and macrophytes), while the allochthonous input (e.g., refractory products of higher plants) is transported into the sedimentary environment by, among other things, water, wind, ice and human agency [*Brassell et al.*, 1978]. Major changes in these parameters are expected with RSL change and may be reflected in TOC.

[11] The presence or absence of cellulose in the plant sources of organic matter deposited in sediments of coastal basins influences the C_{org}/N ratio of the sediments. Nonvascular aquatic plants have low C_{org}/N ratios, typically between 4 and 10, whereas vascular land plants, which contain cellulose, have C_{org}/N ratios of 20 or more [*Meyers and Ishiwatari*, 1993a; *Müller and Mathesius*, 1999]. C_{org}/N ratios have been applied in several investigations of marginal basin sediments [*Chivas et al.*, 2001; *Mackie et al.*, 2005; *Müller and Mathesius*, 1999]. In coastal basins where the contribution of organic matter from vascular land plants is small relative to water column production, the sediments could show lower C_{org}/N ratios than those with higher relative inputs of vascular plant detritus. However, such a simple model of the factors influencing C_{org}/N ratios is not always applicable. High C_{org}/N ratios atypical for algal source OC have been measured in OC rich Mediterranean sapropel layers, late Neogene sediments from the Benguella upwelling region, Eocene horizons from the Arctic Ocean and Cenomanian-Turonian black shales [*Meyers*, 1990; *Stein and Macdonald*, 2004; *Stein et al.*, 2006; *Twichell et al.*, 2002]. In these sediments, the high C_{org}/N ratios are explained by the fact (1) that algae are able to synthesize lipid-rich OC during times of abundant nutrient supply and/or (2) that during sinking, partial degradation of algal OC may selectively diminish N-rich proteinaceous components, and raise the C_{org}/N ratio [*Meyers*, 1997]. Additional high C_{org}/N ratios have also been determined in lake sediments

Table 2. Summary Data for Modern Basins

Basin	Theoretical Stage of Isolation (Figure 1)	Position (Latitude, Longitude)	Type of Environment	Sill Altitude (m OD[a])	High-Tide Altitude (m OD) MHWST[b]	High-Tide Altitude (m OD) HAT[c]	Maximum Depth at High Tide (m)	Salinity Range (psu) (Mean)	Site Number (Figure 3)
Loch nan Ceall	1 and 2	56°90′94N, 5°88′07W, and 56°90′69N, 5°85′36W	open sea loch	na	2.4	3	17.4	33	1, 2, and 3
Rumach tidal pond	3	56°89′84N, 5°89′56W	saline lagoon/pond	0.27	2.4	3	1.9	7 to 33 (28)	4
Craiglin Lagoon	4	56°03′15N, 5°57′09W	saline lagoon	1.417	1.3	1.6	1.60	15 to 33 (20)	6
Loch nan Eala	5	56°90′63N, 5°83′13W	fresh water loch	15.27	2.4	3	4	fresh	5
Loch nan Corr	5	57°23′39N, 5°40′94W	fresh water loch	2.7	2.6	3.2	2	fresh	7

[a] The spot height of the sill above the Ordnance Datum (OD) on UK ordinance survey maps. OD is equivalent to mean sea level (MSL), defined as the MSL at Newlyn in Cornwall between 1915 and 1921.
[b] MHWST, mean high-water spring tides altitude; HAT, highest astronomical tide altitude.
[c] Sample lost.

and related to significant contribution of freshwater Botryococcus-type algae [*Fuhrmann et al.*, 2003].

2. Materials and Methods

2.1. Site Descriptions and Sampling

[12] The sampling strategy was designed to meet the aim of this paper: to investigate the distribution of the alkenones, alkenoates and bulk organic properties in modern and fossil sites that are analogous to the theoretical stages of isolation illustrated in Figure 1.

2.1.1. Modern Basins

[13] The relevant isolation stage (IS) for a particular basin is first determined by comparing the height of the sill with local tidal data. Direct hydrographic measurements are taken to determine changes in salinity, temperature and density (and thus marine incursion) during the tidal cycle for a spring tide, neap tide and a midcycle tide. Individual site descriptions are given in EA-2 in Text S1 and in further detail in the work by *Bendle* [2003]. Summary details of the modern sites and their isolation stage are listed in Table 2, and the locations are indicated in Figure 3; a series of larger-scale site maps are included in the auxiliary material (EA-3 to EA-6 in Text S1). Sediment samples were collected by a sediment grab deployed by wire from a small boat or in the case of Rumach tidal pond collected by hand during low tide. Samples were kept frozen at −20°C until analysis.

2.1.2. Fossil Basins

[14] Details of the analytical procedures used to obtain and radiocarbon date microfossil records and derive the resulting sea level index points from the fossil isolation basins are described by *Shennan et al.* [2000] and references therein. Briefly, for each fossil basin, a series of boreholes were drilled to reconstruct a profile of the basin stratigraphy. One core location was selected to represent the sequence and resampled to provide sediment for further analysis. Core and basin sill altitude were leveled to ordinance datum (OD) using an automatic level. Lithostratigraphy, pollen, diatom, foraminiferal and radiocarbon analyses were prepared using standard procedures [*Moore and Webb*, 1978; *Palmer and Abbott*, 1986; *Scott and Medioli*, 1980; *Troels-Smith*, 1955]. Cores were sealed and refrigerated during the interim between the original microfossil and subsequent subsampling for lipid biomarkers. Details for the fossil basin sediment cores and (where relevant)
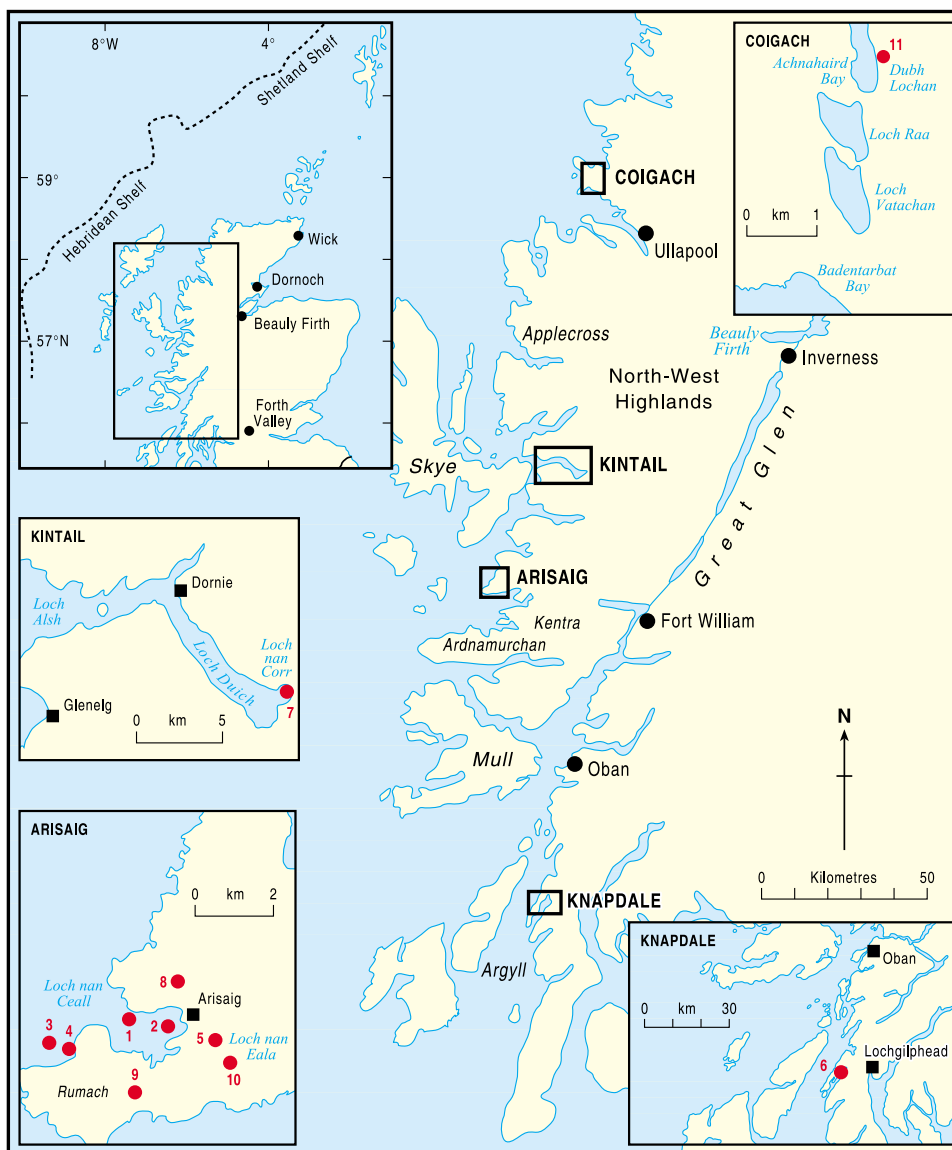
Figure 3. Location map of the field study region. Insets show locations of the study areas with the individual sites indicated. See Tables 2 and 3 for details of each site corresponding to the site number.

Table 3. Summary Data for Fossil Basins

Basin	Relative Sea Level History	Position (Latitude, Longitude)	Sill Altitude (m OD)	Reference	Site Number (Figure 3)
Cnoc Pheadir	above marine limit?	56°91′57N, 5°84′48W	42	*Shennan et al.* [2005]	8
Torr a' Bheithe	late Devensian RSL fall	56°88′90N, 5°86′34W	35.2	*Shennan et al.* [2000, 2005]	9
Loch Dubh	late Devensian RSL fall	56°89′68N, 5°82′28W	20.5	*Shennan et al.* [2000, 2005]	10
Dubh Lochan	early Holocene RSL rise through late Holocene RSL fall	58°06′29N, 5°35′21W	5.7	*Shennan et al.* [2000]	11

the references for the previously published RSL history are given in Table 3.

2.2. Experimental Procedure

2.2.1. Alkenone/Alkenoate Analysis

[15] 36 sediment samples were freeze dried and ground (dry weight ~0.5 to 5g), an internal standard added, and extracted with dichloromethane/methanol at 70°C for 5 min using a MARS 5 microwave extractor (see *Kornilova and Rosell-Melé* [2003] for details). The solvent extract was concentrated to dryness with a centrifugal evaporator or with nitrogen blow down, redissolved in dichloromethane and dried with Na_2SO_4. The extracts were fractionated by preparative liquid chromatography. This was performed using a Thermo Hypersil column (50 × 4.6 mm) packed with Lichospher Si100 5 m silica, and a Thermo Hypersil guard column. Fractions were collected using a Foxy Jr automatic collector. The solvent program was adapted from *Schulz et al.* [2000]. Four fractions were collected in test tubes by eluting at 1 mL min^{-1} with hexane (1.4 mL, aliphatic and cyclic alkanes), hexane/dichloromethane (17:3; 3.5 mL, aliphatic ketones), dichloromethane (2.25 mL, cyclic ketones), acetone (2.25 mL, sterols, alcohols and polars). Fractions 1 and 2 were combined, dried under nitrogen and derivatized using bis-trimethylsilyl-trifluoroacetamide.

[16] Quantification of the absolute abundance of alkenones and alkenoates was performed using a Fisons 8000 Series gas chromatograph fitted with a flame ionization detector (GC-FID) and a split/splitless injector. Baseline separation of the alkenones was obtained using a SGE BP-1 fused silica column (60 m length × 0.25 mm i.d., 0.25 μm film thickness), and an oven temperature program as follows: 60°C for 1 min, 60°C to 200°C at 20°C min^{-1}, 200°C to 305°C at 6°C min^{-1}, held at 305°C for 35 min, 305°C to 320°C at 15°C min^{-1} and held at 320°C for 2 min. Hydrogen was used as a carrier gas.

[17] The concentrations of alkenones in the majority of the samples was extremely low compared to typical samples from deep sea sediments, with concentrations often less than the minimum of 1ng/μl of injected sample previously suggested for accurate peak measurement, when using GC-FID [*Rosell-Melé*, 1994], and the 10ng/μl suggested for accurate estimation of within-class distributions [*Grimalt et al.*, 2001]. In this study (for within-class distributions), this problem was circumvented by using gas chromatography–chemical ionization–mass spec-

trometry (GC-CI-MS). At the time of the analysis for the NW Scottish samples the GC-CI-MS had a detection limit of ~10pg/μl for the quantification of alkenones (linear response between ~20pg/μl and ~20ng/μl); that is, it was two orders of magnitude more sensitive than GC-FID. GC-CI-MS was performed using a Varian 3400 gas chromatograph directly coupled to a Finnigan MAT TSQ 700 triple stage quadrupole mass spectrometer (GC-CI-MS), using ammonia chemical ionization [*Rosell-Melé et al.*, 1995]. The GC was fitted with a PTV injector operated in high-performance nonvaporizing mode, held at 80°C during injection then rapidly heated from 80 to 300°C at 200°C min^{-1}. Separation of the analytes was achieved using a 50 m, 0.32 mm i.d. fused silica column, with 0.12 μm CPSIL5-CB film thickness (Chrompack). The oven temperature program was: 200–300°C at 6°C min^{-1} with no initial hold time and a final isothermal period of 10 min.. Hydrogen was employed as a carrier gas with a head pressure of 8 psi (55 kP). Operating conditions for the mass spectrometer were optimized for sensitivity with respect to the C_{37} methyl alkenones. Chemical ionization was achieved using high-purity ammonia (BOC micrographic grade). Specific ions corresponding to the $[M+NH_4]^+$ species of the analytes were monitored.

[18] Procedural and analytical reproducibility was determined for the analyses with a homogeneous sediment standard (analyzed once for every 10 samples to be validated). The reproducibility of the measurement of total concentrations of alkenones and alkenoates by GC-FID was 5.92% (coefficient of variation (CV) at 2 s.d.). For GC-CI-MS the reproducibility of $U_{37'}^K$ was 0.017 (2 s.d. of $U_{37'}^K$ units) and the reproducibility of %$C_{37:4}$ was 0.79% (2 s.d. of %$C_{37:4}$ units).

2.2.2. TOC and C_{org}/N

[19] Following removal of carbonate (using hydrochloric acid) and water from 1 mg of sample, determination of TOC and C_{org}/N was performed on an elemental analyzer EA1108 (Carlo Erba Instruments). The average reproducibility was: 0.25% (2 s.d.) for TOC and 1.42 C_{org}/N units (2σ) for C_{org}/N.

3. Results and Discussion

3.1. Modern Basins

3.1.1. Alkenone and Alkenoate Abundances

[20] $C_{37:2}$ + $C_{37:3}$ alkenones (ng/g dry sediment) range from undetectable in the freshwater lochs
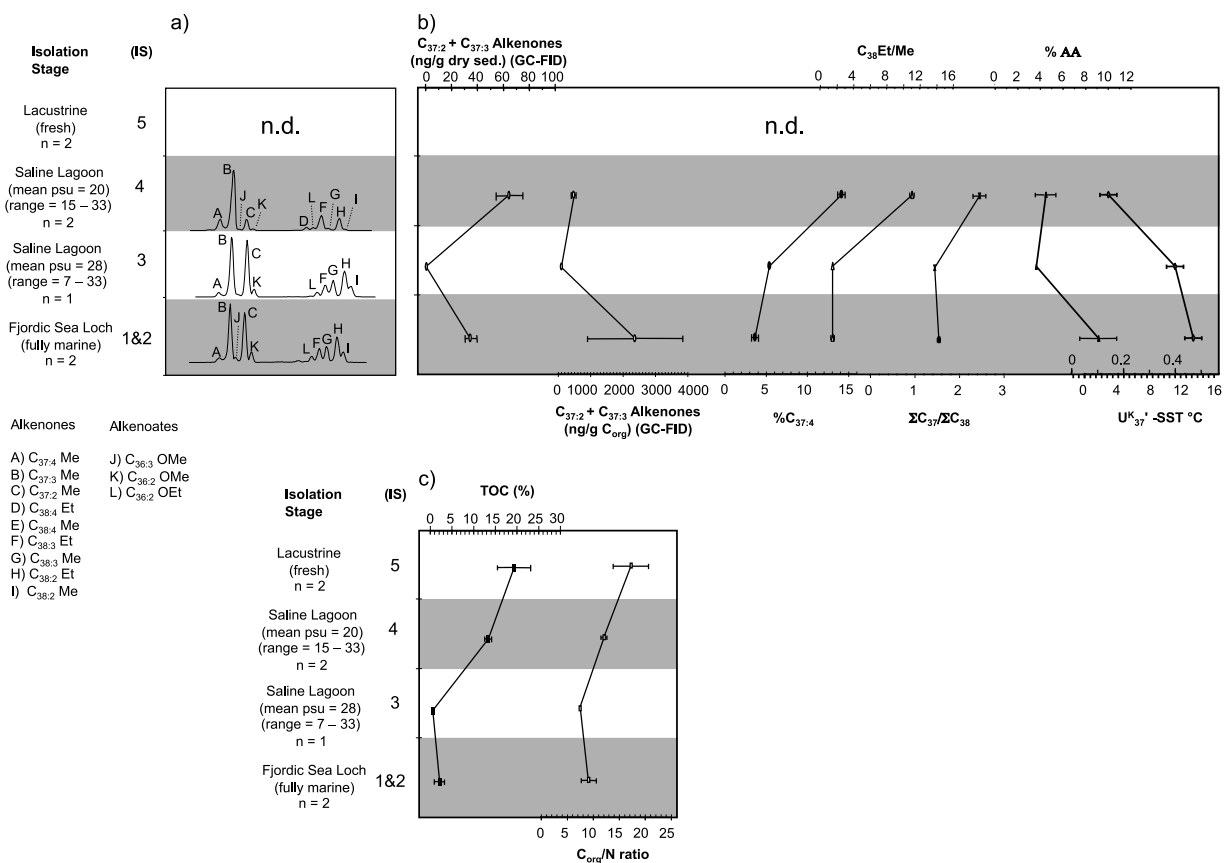
Figure 4. Trends in measured alkenone and alkenoate and bulk organic properties in modern isolation basins in NW Scotland. See Table 2 for basin summary data. Isolation stage (IS) 1 and 2, Loch non Ceal; IS 3, Rumach Tidal Pond; IS 4, Craiglin Lagoon; IS 5, Loch nan Eala and Loch nan Corr. (a) Alkenone and alkenoate fingerprints (GC-CI-MS total ion chromatograms). (b) Alkenone and alkenoate distributions. (c) Bulk organic properties. Alternating shaded and unshaded bands indicate theoretical isolation stages. The data points are means of several samples; the bars indicate minimal and maximal measurements, not error.

(corresponding to IS 5) to 75 ng/g dry sediment in Craiglin (IS 4). Alkenones are detected in all sites that receive inputs from marine waters. The overall trend is a decrease in concentrations between IS 1 and 2 on the one hand, and IS 3 on the other, followed by a sharp increase at IS 4 (Craiglin) and a drop to undetectable levels in the fully isolated IS 5 (freshwater lochs) sites (Figure 4). Normalization to TOC has a noticeable effect on the alkenone concentrations: the trend in $C_{37:2} + C_{37:3}$ concentrations between the IS 1 and 2 and IS 3 sites are reversed, so that the highest values are observed in the open sea loch samples (Figure 4b). However, values at Rumach tidal pond remain lower than those at Craiglin, so that the overall trend of values for $C_{37:2} + C_{37:3}$ is a large decrease from IS 1 and 2 to IS 3, followed by a small increase to IS 4 and then a drop to undetectable values in IS 5.

[21] The strong variations in alkenone concentrations is related to their production by haptophyte algae and the preservation or dilution of the molecules in the sedimentary matrix. Considerable variation in these parameters is expected for the sample sites. A survey of algal species in Craiglin lagoon reports no known alkenone producers and no haptophyte species [*Covey et al.*, 1998]. However, with regard to algal production, the ubiquitous alkenone producer *E. huxleyi* is known to populate fjords in Norway [*Conte et al.*, 1994a], Skagerrak and the Baltic sea [*Blanz et al.*, 2005] and the continental shelf seas of the UK and New England [*Marlowe et al.*, 1984]. Studies of surficial sedimentary and water column alkenone distributions across a salinity transect in the Baltic sea, from fully marine Atlantic source waters to brackish water, shows decreasing concentrations of C_{37} alkenones toward the more brackish regions, where an unconfirmed alkenone producer may exist [*Blanz et al.*, 2005; *Schöner*, 2001; *Schulz et al.*, 2000]. Two possible producers of alkenones in coastal/brackish waters are *Chrysotila lamellosa* and *Isochrysis galbana* [*Conte et al.*,

1994b; *Marlowe et al.*, 1990; *Parke*, 1949; *Rontani et al.*, 2004] although *Isochrysis* strains are also known from oceanic waters [*Versteegh et al.*, 2001]. For many lacustrine sites, alkenone producers have not been identified. However, from culture experiments the noncalcifying species *C. lamellosa Anand* has been inferred as the producer of alkenones in Lake Xiarinur (Inner Mongolia, China) [*Sun et al.*, 2007] while in a series of lakes in Greenland a unique "Greenland phylotype" of haptophyte algae is inferred based on analysis of 18S ribosomal DNA sequences, but the precursor organism has not yet been isolated and identified [*D'Andrea and Huang*, 2005; *D'Andrea et al.*, 2006]. In fact, alkenones are not found in all lacustrine sediments, and the physical or nutrient controls on their lacustrine distributions are not known.

[22] If the major control on the sedimentary concentrations of the $C_{37:2} + C_{37:3}$ alkenones is in situ production by *E. huxleyi*, we would predict the highest concentrations of alkenones within the fjordic sea lochs, with decreasing values in the brackish basins and with unpredictable results for the freshwater lochs. This trend would be reproduced if an alternative driver of alkenone sedimentary concentrations was the advection of alkenones from fully marine Atlantic source areas. Again higher values would be predicted in the openly ventilated fjordic sea lochs, with lower values expected for the sites of restricted marine circulation, especially for IS 4 (Craiglin lagoon) which is only ventilated by marine waters during some high spring tides. Some of the variation in the concentrations of the alkenones in the modern sites may result from differences in preservation due to sedimentary or water column oxygen content. Investigation of the hydrographic regime at Loch nan Ceall (IS 1 and 2), Rumach tidal pond (IS 3) and Craiglin (IS 4) reveals that the water column of the former two is well mixed and oxygenated, while at Craiglin there is at least seasonal stratification and sediment/water interface anoxia [*Bendle*, 2003]. Degradation rates for alkenones in sedimentary samples are higher in oxic than in anoxic conditions [*Gong and Hollander*, 1999; *Madureira et al.*, 1995; *Sun and Wakeham*, 1994], and that may explain the relative increase in alkenone abundance between IS 3 and IS 4 (Figure 4).

3.1.2. Alkenone and Alkenoate Within-Class Distributions

[23] Within-class distributions refers to the occurrence and relative abundance of specific alkenones (or alkenoates) measured against other components within the same chemical class (e.g., ratios of one type of alkenone or alkenoate to another). The alkenone and alkenoate fingerprints for the modern NW Scottish surface sediments are illustrated by the GC-CI-MS total ion chromatograms in Figure 4a. There is a distinct difference between the distribution patterns observed in IS 1 and 2 (Loch nan Ceall) and IS 3 (Rumach tidal pond) and that observed in IS 4 (Craiglin). This distinction compares interestingly with the alkenone distributions in the Baltic sea [*Blanz et al.*, 2005; *Schöner*, 2001; *Schulz et al.*, 2000] and in various lakes [*Chu et al.*, 2005; *Zink et al.*, 2001]; in this study, the alkenone patterns in IS 1 to 3 (Loch nan Ceall and Rumach tidal pond) resemble a typical North Atlantic/western Baltic pattern produced by *E. huxleyi* while the alkenone pattern in IS 4 (Craiglin) resembles *Schulz et al.*'s [2000] reported pattern II from the eastern Baltic Sea (salinity < 7.7 psu) with distinctly higher $C_{37:4}$ abundance, lowered abundance of $C_{37:2}$ and very low abundance of C_{38} methyl alkenones. Within the eastern Baltic Sea it is suggested that the alkenones are produced by an unknown organism rather than *E. huxleyi* [*Blanz et al.*, 2005; *Schulz et al.*, 2000]. Moreover, elevated $%C_{37:4}$ and a lack of $C_{38:Me}$ alkenones has been proposed as characteristic of the genera *Chrysotila* and *Isochrysis* [*Conte et al.*, 1994b].

[24] Thus the alkenone distributions are likely a function of physiological response to environmental conditions (such as temperature, salinity, or nutrient availability) by alkenone producers, and inputs from different haptophyte populations with a distinct biochemical signature. Postdepositional bias seems unlikely given the bulk of evidence which suggests modifications of alkenone ratios are rarely serious even when the concentrations of C_{37} alkenones are severely depleted [*Grimalt et al.*, 2000, and references therein].

[25] One or both of these factors is likely to control the alkenone distributions in the isolation basins. *Blanz et al.* [2005] suggested that in the Baltic Sea a combination was operating; with changing biosynthesis of alkenones by the coccolithophore *E. huxleyi* as it responds to changing salinity, combined with a contribution of alkenones by an unidentified organism (possibly genera *Chrysotila* and/or *Isochrysis*) in the lowest-salinity regions. It is likely that similar processes are operating across the range of isolation basins in this study. Detailed microbial surveys and environmental monitoring will be needed to determine the environmental and

biological controls on coastal biomarkers in future studies.

[26] It can, at least, be stated that the divergence in alkenone patterns over the relatively small study area is unlikely to be a physiological response of *E. huxleyi* producers to changes in ambient water temperature alone. $U^K_{37'}$ ranged from 0.13 in Craiglin to 0.48 in Loch nan Ceall. Converted to sea surface temperature (SST) using the calibration of *Müller et al.* [1998] the alkenone-SST estimates for Loch nan Ceall and Rumach tidal pond give values of ~11 to 13°C (see Figure 4b), which compare very well with mean annual World Ocean Database values for the region [*Conkright et al.*, 1998]. So the alkenone-SST estimates from these two sites, which are well ventilated by marine waters, are realistic. However, the samples from the brackish Craiglin lagoon give alkenone temperature estimates of 2.6°C to 3°C. These are not realistic: in fact Craiglin had the warmest surface waters of the sites measured during sample collection in 2002 (August: ~20°C; October: ~17°C). This failure of the alkenone-SST proxy in the Craiglin lagoon samples is not surprising given that we apply a calibration based on marine samples, but the alkenone fingerprint in Craiglin is nonmarine, characterized by distinctly higher $C_{37:4}$ abundance and very low abundance of C_{38} methyl alkenones.

[27] The observations of $U^K_{37'}$-SST estimates in the NW Scottish coastal environments support previous evidence that SSTs derived from $U^K_{37'}$ measurements in shallow coastal environments should be treated with caution [*Conte et al.*, 1994a; *Ficken and Farrimond*, 1995]. Specifically, attention should be paid to the within-class distributions to assess if the fingerprint resembles that normally associated with production in the open ocean. In other words, if the paleoenvironment had open ventilation to a fully marine continental shelf then the resulting alkenone-SST estimates may be realistic, but alkenone-SST estimates from reduced salinity, lagoonal environments are unreliable.

[28] %$C_{37:4}$ ranges from 3.3% for Loch nan Ceall station 2 to 14.6% at Craiglin station 1, with a general trend toward higher values with increasing basin isolation (Figure 4b). The samples from IS 1 to 3 (Loch nan Ceall and Rumach tidal pond) are between 3 and 5% which is typical for North Atlantic alkenones found in open marine conditions. The highest values of ~14% are from Craiglin lagoon, which has brackish waters (water column average salinity of ~24 psu (s.d. 3 psu)

when measured on several occasions in August and October 2002). None of the %$C_{37:4}$ values exceed 17%, which is the highest value of %$C_{37:4}$ previously found to be produced by *E. huxleyi* in a fjord [*Conte et al.*, 1994a]. No %$C_{37:4}$ values in the modern basin samples approach the higher values (typically ~20% up to 95%) reported for lakes, polar ocean waters or the <7.7 psu waters of the Baltic Sea [*Bendle et al.*, 2005; *Chu et al.*, 2005; *Schulz et al.*, 2000; *Volkman et al.*, 1988].

[29] The ratio of C_{38} methyl to C_{38} ethyl alkenones (C_{38}Et/Me) was noted by *Schulz et al.* [2000] to vary noticeably in sediments from a salinity gradient across the Baltic Sea, C_{38} methyl alkenone being undetectable in the samples from the fresher regions. In the modern NW Scotland samples, values of C_{38}Et/Me are ~2 in the samples from IS 1, 2 and 3 but jump to ~11 in the samples from IS 4, representing an approximately fivefold decrease in the relative abundance of the C_{38} methyl to the C_{38} ethyl alkenones (Figure 4b). There is also a sudden increase in $\Sigma C_{37}/\Sigma C_{38}$ from IS 1, 2 and 3 to IS 4 which partially reflects the decrease in the C_{38} methyls in the IS 4 (Craiglin) samples (Figure 4b).

[30] Variability is also observed in the ratio of alkenoates to alkenones. %AA ranges from 3.6% in Craiglin to 10.8% in Loch nan Ceall (Figure 4b). In general, %AA is higher in IS 1 and 2 than in the other samples, while there is no trend in %AA between the IS 3 and IS 5 samples (Figure 4b). As for the other measures of within-class distributions the variation across the sites for %AA may be a physiological response to environmental stress (salinity, nutrient availability), or a product of different haptophyte populations. However, the interpretation of %AA may be vulnerable to diagenetic bias, as alkenoates have been shown to be less resistant to degradation than alkenones [*Teece et al.*, 1998].

3.1.3. TOC and C_{org}/N

[31] The modern basin samples display a very wide range in values of TOC, from 0.6% in Rumach tidal pond, to 23.5% in Loch nan Corr (Figure 4c). There is a general increase in TOC with isolation. Thus, the IS 5 sediments contain the highest values of TOC (15.2% in Loch nan Eala; 23.5% in Loch nan Corr) and there is a marked increase in TOC between the sediments of the exposed Rumach tidal pond (IS 3) and the highly sheltered Craiglin lagoon (IS 4). However, there is a slight decrease in TOC between IS 1 and 2 (the fjordic sea loch
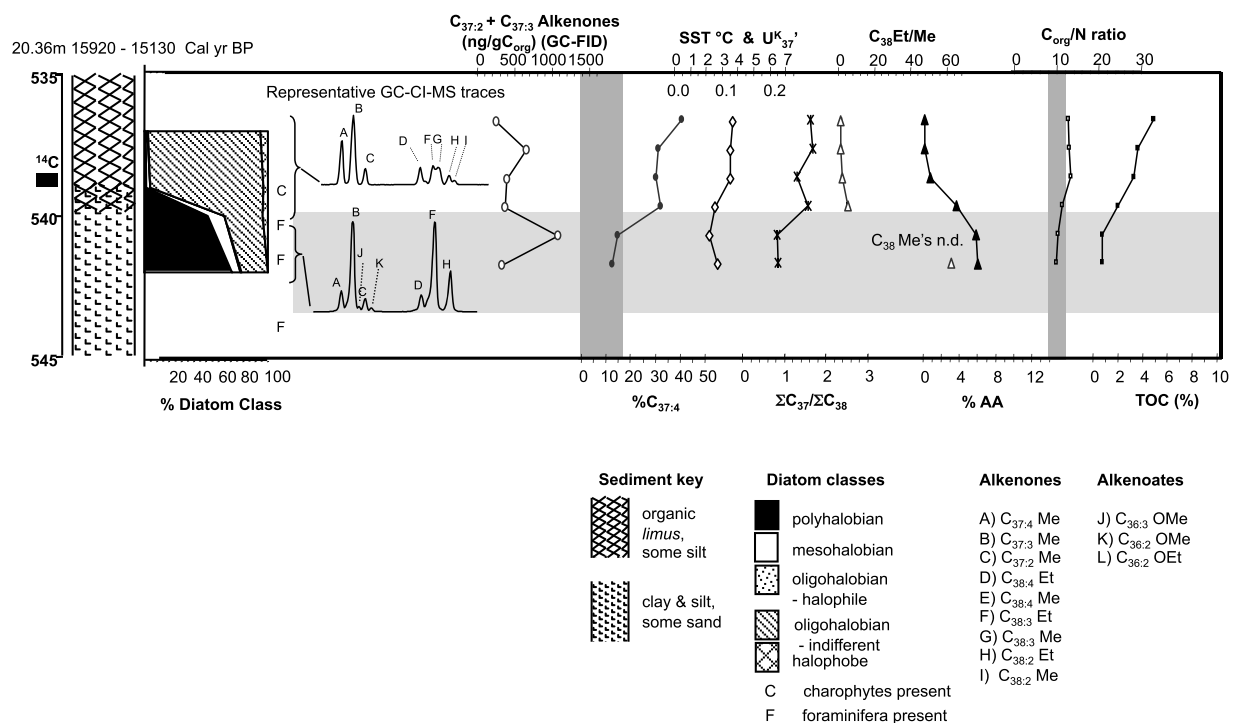
Figure 5. Loch Dubh (site 10 in Figure 3 and Table 3) alkenone and microfossil summary. The altitude refers to the rock sill of the basin. The date comes from the transition from clastic sediment to organic limus. The horizontal shaded area delimits the marine phase according to the microfossils (diatoms, foraminifera, and charophyte oogonia). The vertical shaded area in the $\%C_{37:4}$ plot represents values <17%, i.e., below the upper limit of $\%C_{37:4}$ known to be produced by *E. huxleyi* in sea lochs [*Conte et al.*, 1994a]. The vertical shaded area in the C_{org}/N plot divides predominantly marine (<8) from predominantly terrestrial (>12) organic inputs according to *Müller and Mathesius* [1999].

sediments) and IS 3 (Rumach tidal pond). The increase in TOC with the increasing isolation stages will result from a complex interplay of factors. In this case we have observed that water mass circulation and bottom water oxygen concentrations vary across the basins, and autochthonous and allochthonous carbon inputs may be expected to vary as well.

[32] Values of C_{org}/N from the modern basins display a range from 7.5 in Rumach tidal pond to 20.1 in Loch nan Eala, with values decreasing slightly from IS 1 and 2 to IS 3 and increasing with isolation through IS 4 and 5 (Figure 4c). *Müller and Mathesius* [1999] used values of C_{org}/N and $\delta^{13}C$ to reconstruct marine versus lacustrine phases in fossil lagoons from the southern Baltic Sea. Based on previous work [*Bordovskiy*, 1965; *Prahl et al.*, 1980] they suggested that C_{org}/N above 12 indicated predominantly terrestrial (lacustrine) organic inputs, C_{org}/N below 8 indicated predominantly algal (marine) organic inputs, while C_{org}/N of 8 to 12 indicated mixed inputs. The results from the NW Scotland modern basins seem to confirm

that $C_{org}/N > 12$ may be a useful indicator of RSL change in coastal basins.

3.2. Application to Fossil Isolation Basins

[33] In this section we compare the down-core variation of biomarkers and bulk organic properties with records of established microfossil sea level indicators in sediment cores from NW Scotland fossil basins (Table 3 and Figures 5–8).

3.2.1. Arisaig: Loch Dubh, Torr a'Bheithe, and Cnoc Pheadir

[34] Previous studies have used isolation basins from Arisaig to constrain relative sea level changes back to ~16 kyr ^{14}C BP [e.g., *Shennan et al.*, 1994, 2000, 2005] (see Figure 3, sites 8, 9, and 10, and EA-2 in Text S1). The region was covered with relatively thick ice (~900 m) at the Last Glacial Maximum and the sites form part of a staircase sequence that records the regression from the Last Glacial Maximum marine limit through to an early Holocene minimum in RSL.
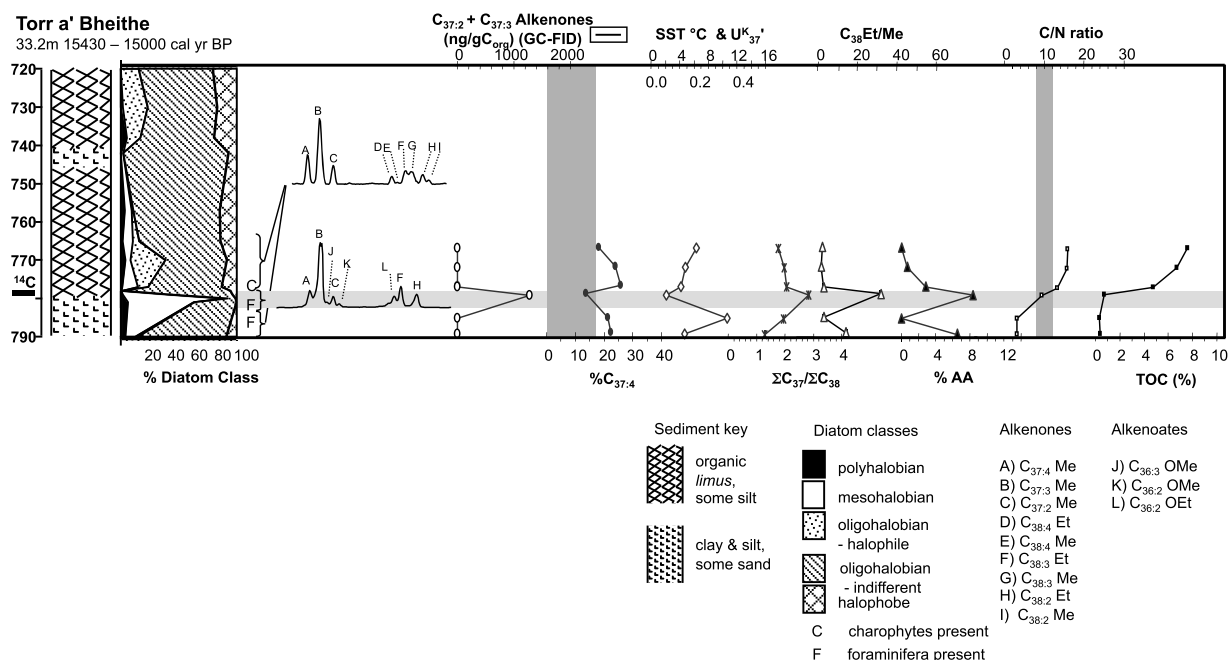
Figure 6. Torr a' Bheithe (site 9 in Figure 3 and Table 3) alkenone and microfossil summary. The altitude refers to the rock sill of the basin. The date comes from the transition from clastic sediment to organic limus. The horizontal shaded area delimits the marine phase according to the microfossils (diatoms, foraminifera, and charophyte oogonia). The vertical shaded area in the %$C_{37:4}$ plot represents values <17%, i.e., below the upper limit of %$C_{37:4}$ known to be produced by *E. huxleyi* in sea lochs [*Conte et al.*, 1994a].

3.2.1.1. Loch Dubh

[35] The results of the biomarker and bulk organic geochemical analysis for Loch Dubh (site 10 in Figure 3) are given in Figure 5 together with results of previous lithostratigraphic, microfossil and dating work [*Shennan et al.*, 2000]. The previously reported diatom data show a rapid transition from marine to freshwater conditions between 540 and 539 cm depth. Alkenones are detected in all samples including the fully isolated sediments above 539.7 cm depth (250 to 650 ng/g C_{org}). Concentrations of $C_{37:2} + C_{37:3}$ alkenones peak at 1082 ng/g C_{org}, below the diatom isolation contact. This peak may be due to changes in conditions (e.g., reduction in tidal energy, decrease in oxygen) to an environment closer to the modern Craiglin lagoon (IS4) which favors the preservation of alkenones (Figure 4b). Concentrations then fall to ∼380 ng/g C_{org} across the diatom isolation contact (from 540.7 to 539.7 and 538.7 cm) suggesting a sharp fall in alkenone concentration during the final marine isolation (IS4 to IS5).

[36] The alkenones in the core are distinguished by two distinct within-class distribution patterns, with the bottom two samples (541.7 to 540.7 cm) having %$C_{37:4}$ < 15%, and a high C_{38}Et/Me ratio (C_{38}

methyls were undetected at 540.7 cm). This pattern is comparable to the modern, brackish Craiglin lagoon (IS 4). In the samples from 539.7 cm upward in the core, the alkenone distribution pattern is distinguished by %$C_{37:4}$ > 30%, a fall in the ratio of C_{38}Et/Me and an increase in $\Sigma C_{37}/\Sigma C_{38}$. This distribution pattern compares to observations made in lacustrine environments in northern Europe [*Cranwell*, 1985; *Zink et al.*, 2001], especially the high %$C_{37:4}$. The %AA is highest in the bottom two samples (541.7 and 540.7 cm) at ∼6%, intermediate at 539 cm at 3.7%, and lowest in the top three samples (538.7 to 536.7 cm) with <1%. This trend compares with the modern samples, in which %AA was observed to decrease with isolation. $U^K_{37'}$ shows some variation (0.11 to 0.17) up the core. The bottom two samples (assumed to be the marine phase) give cold SSTs of 2.6 and 2.1°C. This may be a reasonable estimate for waters proximal to an ablating ice sheet at 15500 Cal yr BP. The earliest foraminiferal SST estimates from the Barra Fan (located at the continental shelf ∼100 km west of Arisaig) date from 15,000 Cal yr BP and are ∼4°C (±2°C) (summer SST, SIMMAX method [*Kroon et al.*, 1997]).

[37] Bulk TOC increases steadily throughout the section of core studied. The C_{org}/N ratio increases from 541.7 to 538.7 cm suggesting steadily increasing inputs of organic matter of terrestrial
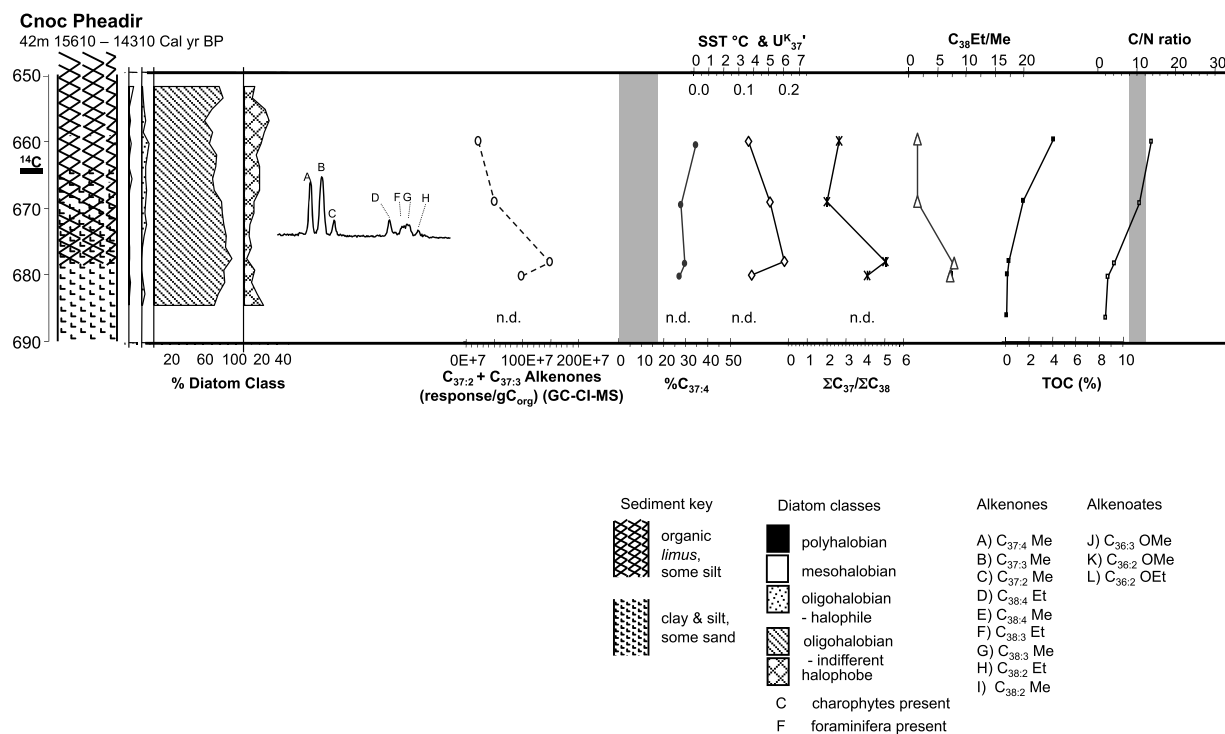
Figure 7. Cnoc Pheadir (site 8 in Figure 3 and Table 3) alkenone and microfossil summary. The altitude refers to the rock sill of the basin. The date comes from the transition from clastic sediment to organic limus. The shaded area in the %$C_{37:4}$ plot represents values <17%, i.e., below the upper limit of %$C_{37:4}$ known to be produced by *E. huxleyi* in sea lochs [*Conte et al.*, 1994a].

source relative to algal inputs over this period. Values of $C_{org}/N > 12$ (considered to be typical of terrestrial values [*Bordovskiy*, 1965]), coincided with the diatom isolation contact at 539.7cm.

3.2.1.2. Torr a'Bheithe

[38] The form of the transition from marine to freshwater conditions in Torr a'Bheithe (site 9 in Figure 3) as recorded by diatoms contrasts with Loch Dubh, in that there is just a brief spike in marine conditions before isolation between 779 and 777 cm depth (Figure 6). Values for $C_{37:2} + C_{37:3}$ recreate this rapid marine transgression and subsequent isolation, as observed in the diatoms. This is characterized by maximal concentrations of 1284 ng/g C_{org} at 779 cm by GC-FID, with alkenones below detection limits for all the other samples. However, alkenones (and the within-class distributions) are measurable for the other samples by GC-CI-MS, although at a low response level compared with the sample at 779 cm. The alkenones in the core are distinguished by two distinct within-class distribution patterns. In the marine phase, %$C_{37:4}$ is 13.4%, C_{38}Et/Me and $\Sigma C_{37}/\Sigma C_{38}$ are high due to the very low relative abundance of the C_{38} methyl alkenones. This pattern is similar to

that observed in the marine section of the Loch Dubh core and the pattern from the brackish Craiglin lagoon in the modern samples. In the rest of the core %$C_{37:4} > 18$% and C_{38}Et/Me and $\Sigma C_{37}/\Sigma C_{38}$ are much lower: this pattern is closer to that observed in the lacustrine phase of Loch Dubh and lacustrine samples from northern Europe [*Ficken and Farrimond*, 1995; *Zink et al.*, 2001].

[39] %AA is highest in the marine phase: a value of ~8% is consistent with the modern fully marine observations. Values are generally much lower in the other parts of the core, apart from an increase in the bottom sample which contradicts the inferences from alkenone concentrations and %$C_{37:4}$. $U_{37'}^{K}$ shows considerable variation (0.12 to 0.4) up the core. The value for the marine phase gives a cold SST of 2.1°C. This is similar to the results from Loch Dubh and again is a very cold estimation. TOC increases sharply at 779 cm, while the C_{org}/N ratios surpassed 12 (considered to be typical of terrestrial values [*Bordovskiy*, 1965]) at 779 cm, coinciding with the isolation contact.

3.2.1.3. Cnoc Pheadir

[40] Cnoc Pheadir (site 8 in Figure 3) is a basin from the top of the Arisaig staircase sequence. A
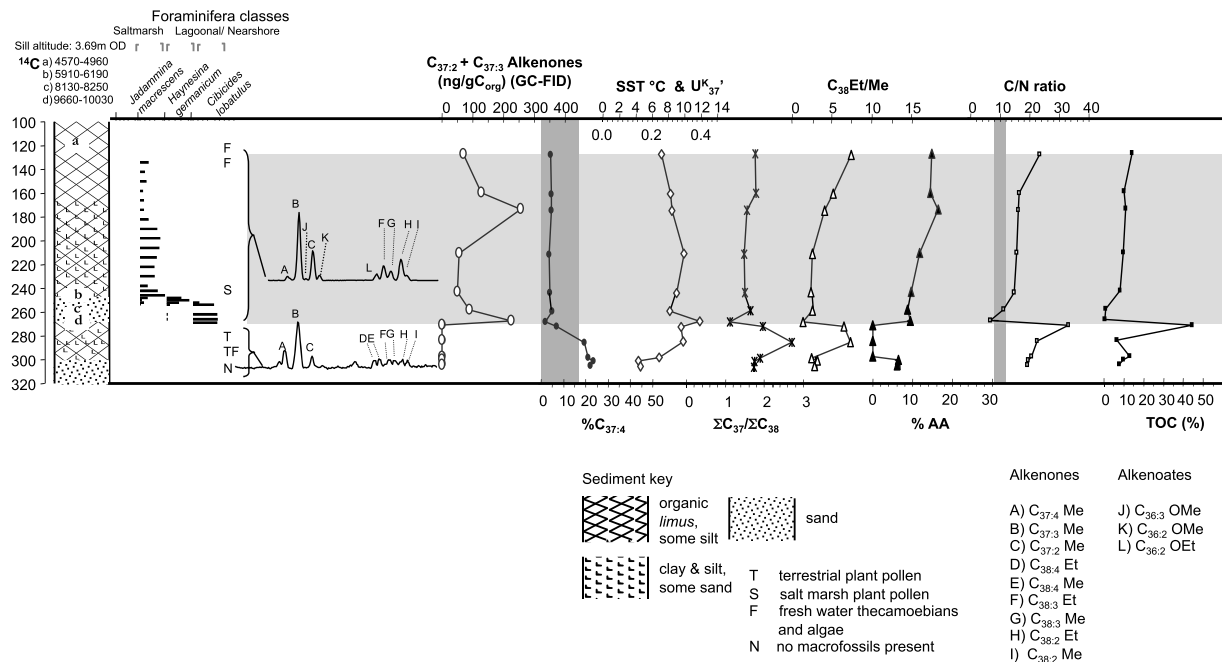
Figure 8. Dubh Lochan (site 11 in Figure 3 and Table 3) alkenone and microfossil summary. The altitude refers to the rock sill of the basin. Foraminifera salinity classes illustrate the degree of marine incursion into the basin. Radiocarbon dates are shown as calibrated age ranges. The horizontal shaded area delimits the marine phase according to the microfossils (pollen and thecamoebians). The vertical shaded area in the %$C_{37:4}$ plot represents values <17%, i.e., below the upper limit of %$C_{37:4}$ known to be produced by *E. huxleyi* in sea lochs [*Conte et al.*, 1994a].

core from the basin shows a transitional lithostratigraphy superficially similar to the marine-terrestrial sequences identified in the lower basins of the Arisaig staircase. If this were a genuine marine-terrestrial transition, it would be evidence of a new local marine limit of 42 m OD. However, the diatom assemblages suggest freshwater conditions throughout all depths of the core [*Shennan et al.*, 2005] (Figure 7) and so the sea level history of the site is somewhat ambiguous.

[41] Alkenones are only measurable by GC-FID in the top sample of the core with $C_{37:2}$ + $C_{37:3}$ at 178 ng/g C_{org}. Measurement by GC-CI-MS detected alkenones in all of the samples except the bottom sample at 686 cm. %$C_{37:4}$ is high (>27%) throughout the core, substantially higher than the highest values known for *E. huxleyi* production in a sea loch (17% [*Conte et al.*, 1994a]). This supports the diatom evidence that there was no fully marine phase in this basin. $\Sigma C_{37}/\Sigma C_{38}$ and C_{38}Et/Me both display fluctuations up core, while no alkyl alkenoates are detected in any of the samples. $U^K_{37'}$ varies between 0.1 and 0.17 up the core, but as the alkenones are not likely derived from a marine algal producer they are likely to be of no use for paleotemperature estimation.

[42] TOC and C_{org}/N steadily increase up core. It is worth noting that if C_{org}/N were relied on for a paleoenvironmental reconstruction without the alkenone data, then it might be incorrectly suggested that below ∼673 cm the organic carbon was marine in origin. This is based upon the suggestion of *Müller and Mathesius* [1999] that C_{org}/N below 8 indicates dominantly marine carbon inputs.

3.2.2. Dubh Lochan

[43] This site (site 11 in Figure 3) is located in the Coigach region (Figure 3), which contrasts with the Arisaig region: it was well outside the Younger Dryas ice limit and there is no evidence of Late Glacial sea levels higher than at present. The record from Dubh Lochan provides an alternative test for the biomarker methods, because in contrast to a relatively rapid marine–fresh water transition (e.g., Loch Dubh and Torr a'Bheithe) it is interpreted by *Shennan et al.* [2000] to record an early Holocene sea level rise followed by a steady regression and brackish phase until isolation in the mid-Holocene.

[44] $C_{37:2}$ + $C_{37:3}$ are undetectable by GC-FID below 268 cm in the section of the core preceding

the marine transgression identified by the micro-fossil data (Figure 8). Alkenones are detected by GC-CI-MS in this section but the response is weak. At 268 cm ($\sim$9000 Cal yr BP), at exactly the depth where marine foraminifera appear in the core, alkenones become detectable using the less sensitive method by GC-FID with $C_{37:2} + C_{37:3}$ at 225 ng/g C_{org}. Below 268 cm alkenone patterns are characterized by $C_{37:4} > 18\%$, except in the sample immediately below the marine transition at 272 cm which records 7%. $\Sigma C_{37}/\Sigma C_{38}$ and $C_{38}Et/Me$ show increases in the lower unit followed by a sharp fall with the marine transgression. %AA drops from $\sim$7% to 0% in the lower unit before increasing sharply to 9% at the marine transgression.

[45] Above 268 cm the alkenone distributions resemble those associated with production in the North Atlantic by *E. huxleyi*, with %$C_{37:4}$ below 5%. This suggests that the alkenones deposited in the basin were of a fully marine source. According to the foraminiferal data following a lagoonal phase, a saltmarsh environment colonizes, at least, some part of the basin from 245 cm ($\sim$6000 Cal yr BP) upward. There is a decrease in the alkenone abundances associated with the start of this phase but %$C_{37:4}$ remains low. This suggests that either the alkenone production was continuing in situ and the water in the basin must have had consistent fully marine qualities (i.e., the foraminiferal signal must be influenced by marsh at the fringe of the basin) or the alkenones deposited in the basin were imported with marine water across the basin sill while a marsh developed throughout the basin. At 176 cm there is a marked increase in $\Sigma C_{37} + \Sigma C_{38}$ concentrations to the highest values of 254 ng/g C_{org} before values fall to 68 ng/g C_{org} at 130 cm. This peak is not matched by an increase in the abundance of fully marine foraminifera. The discrepancy suggests that the alkenone concentration peak results from either increased local or regional productivity by the precursor (*E. huxleyi*) or greater preservation of alkenones.

[46] $U^{K}_{37'}$ varies from 0.2 to 0.4 down the core. The initial marine incursion value gives a SST estimate of 12°C, which matches present mean annual SST for the continental shelf off Coigach [*Conkright et al.*, 1998] and seems a reasonable estimate for the mid-Holocene. This is followed by a decrease in SST to $\sim$8°C.

[47] TOC and C_{org}/N both show sharp fluctuations associated with the marine incursion. At the marine transgression C_{org}/N falls below 8, to levels considered to be typical of marine organic inputs [*Prahl et al.*, 1980]. Above the transition to the marine phase, there is a steady increase in all the parameters, perhaps associated with the development of a saltmarsh in part of the basin. All the parameters show general increases throughout the upper part of the core, suggesting increasing inputs of terrestrial organic matter over this time.
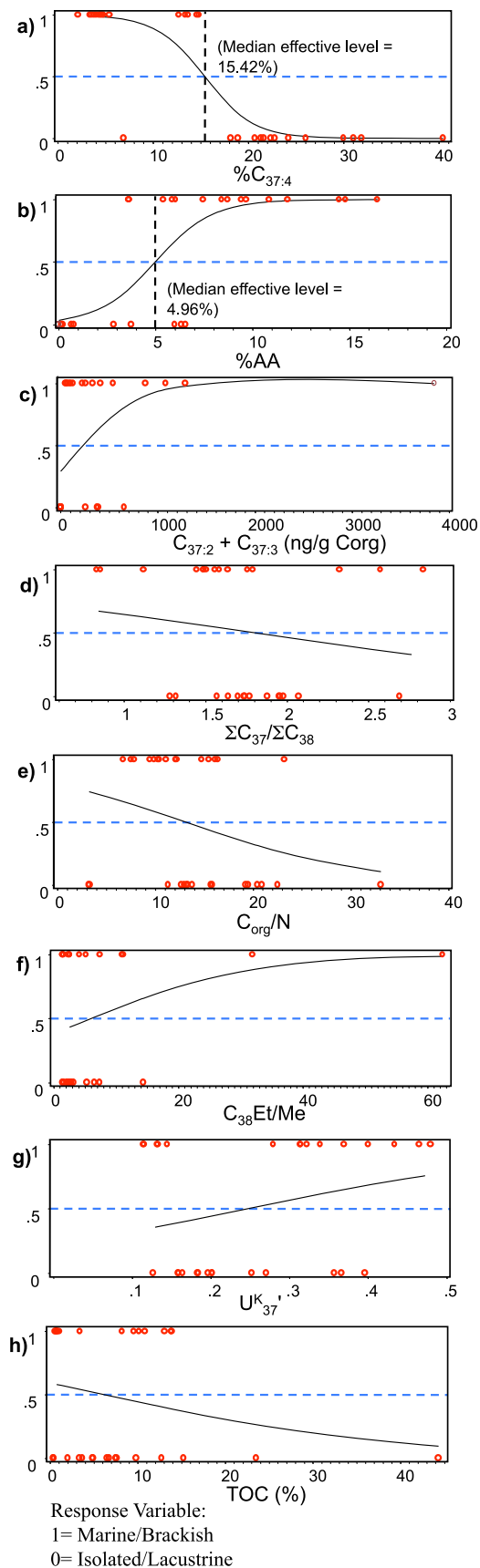
3.3. Logit Regression Analysis

[48] Results of the analyses of sediment samples from the fossil basin and modern sites were combined for statistical analysis. As a precaution the samples from Cnoc Pheadir were not used as the isolation status of the samples is more ambiguous than for the other sites. The efficiency of the organic geochemical variables at discriminating between isolated and marine/brackish phases in all the samples was quantified using logit regression. Given the number of variables (8) and samples (31), statistical analysis is necessary to reach systematic conclusions. Essentially, the aim is to find which explanatory variables (molecular and bulk organic geochemical measurements) can predict the response variable (basin isolation status) with the smallest possible error. The response variable is binary with just two states, i.e., not isolated from the sea (marine/brackish) versus fully isolated from the sea (lacustrine), based on either microfossil indicators (fossil basins) or observation (modern basins). The logit model [*Agresti*, 2002] used to relate the binary response variable *y*, coded as 0 or 1 for the two states, to a quantitative explanatory variable *x* was

$$y = \exp(a + bx)/[1 + \exp(a + bx)].$$

Note that this model may easily be extended to include two or more predictor variables, but as we did not find models with two or more predictors helpful we focus here on the version just given.

[49] The model gives a prediction of the probability of occurrence of the state coded as 1, i.e., the probability of being marine/brackish (rather than lacustrine/isolated). A useful summary level is that value of *x* for which the predicted value of *y* is 0.5, given directly when there is a single predictor by $-a/b$ and here called the median effective level (EL50). This represents the level at which each of the two states has 50% chance of occurrence and so yields a suggested threshold value for the explanatory variable, which could be applied to paleo-RSL studies.

Figure 9. Logit regressions for marine-nonmarine categorization of modern and fossil NW Scottish coastal sediments by various explanatory variables (i.e., organic geochemical and bulk organic measurements). (a) $\%C_{37:4}$, (b) $\%AA$, (c) $C_{37:2} + C_{37:3}$, (d) $\Sigma C_{37}/\Sigma C_{38}$, (e) C_{org}/N, (f) $C_{38}Et/Me$, (g) U^K_{37}', and (h) TOC. Figures 9a–9h are ranked according to their predictive capability (see Table 4 for details). $\%C_{37:4}$ is the most effective variable for predicting the depositional origin of the sediments.

[50] Using Stata statistical software (StataCorp, 2007) a curve was fitted by logit regression for each of the explanatory variables (biomarker concentration, within-class ratio, etc.) to assess their value as a predictor for basin isolation status. The model results are illustrated in Figure 9 and model details are given in Table 4. The results highlight the explanatory variables which show the clearest discrimination of basin isolation status. The only convincing discriminations are by $\%C_{37:4}$ and $\%AA$, illustrated in both cases by a clear fitted sigmoid curve.

[51] The P value, the correlation between observed and predicted values and EL50 were calculated for each of the logit regressions and the results are given in Table 4. The P value is the exact significance level associated with each regression: for example, the decision to reject a null hypothesis when $P < 0.01$ is equivalent to a test using a significance level of 1%. The P values tend to match visual assessments of the logit regressions: at a 1% significance level, null hypotheses can be rejected only for $\%C_{37:4}$, $\%AA$ and $C_{37:2} + C_{37:3}$. The correlation between the values observed for the response and those fitted or predicted from each explanatory variable is a useful general measure of predictive power [*Zheng and Agresti*, 2000]. When squared, that correlation gives an analog of R^2 from conventional regressions. Only $\%C_{37:4}$ (0.87) and $\%AA$ (0.75) gave correlations greater than 0.5; $C_{37:2} + C_{37:3}$ gave a correlation of 0.46. All the other explanatory variables gave correlations between 0.17 and 0.41, indicating poor prediction performance.

[52] Thus only $\%C_{37:4}$ and $\%AA$ do well at predicting whether NW Scottish coastal sediments were deposited under marine/brackish or fully isolated/lacustrine conditions. Furthermore, of these two measures $\%C_{37:4}$ is the stronger candidate on several counts. First, it yielded the more compelling modeling results (see Figure 9 and Table 4). Second, it is stronger on the basis of chemical principles: $\%C_{37:4}$ is based on within-

Table 4. Results of Logit Regression Analysis for Marine/Brackish-Isolated/Lacustrine Binomial Categorization by Explanatory Variables

Explanatory Variable	Number of Observations	b Value	P Value	Reject H_0: Significance 5%	Reject H_0: Significance 1%	Correlation Between Observed and Predicted Values	Median Effective Level (EL_{50})
%$C_{37:4}$	29	−0.3936	0.0000	yes	yes	0.874	15.43
% AA	29	0.6829	0.0000	yes	yes	0.754	4.966
$C_{37:2} + C_{37:3}$ (ng/g Corg)	31	0.0036	0.0050	yes	yes	0.462	245
$\Sigma C_{37}/\Sigma C_{38}$	29	−0.7411	0.0368	yes	no	0.167	1.820
C_{org}/N	31	−0.108	0.1013	no	no	0.293	13.22
$C_{38}Et/Me$	28	0.0784	0.1136	no	no	0.265	5.879
$U^{K}_{37'}$	29		0.1426	no	no	0.267	0.245
TOC	31	−0.0596	0.2119	no	no	0.204	6.305

class variation of C_{37} alkenones, a lipid group for which the consistency of within-class distributions, under differing preservational conditions, has been well documented (as reviewed by *Grimalt et al.* [2000]). %AA is based on the ratio of alkenoates to alkenones: the interpretation of this measure is complicated by observations that alkenoates are a more labile compound class than alkenones [*Teece et al.*, 1998].

[53] From Figure 9 of the logit regression for %$C_{37:4}$ it can be seen that all of the marine samples had %$C_{37:4}$ below 15% and all the lacustrine sediments (from the fossil basins), except one outlier, had %$C_{37:4}$ more than 17%. The outlier (nonmarine, %$C_{37:4}$ of 7%) was a sample immediately below a marine transition. The logit regression produced a median effective level of ~15.5%, which suggests that this level may be used as a threshold to determine the origin of sediments. However, the upper limit of %$C_{37:4}$ known to be produced by *E. huxleyi* in a marine sea loch is 17% [*Conte et al.*, 1994a]. Therefore, we suggest that a more appropriate threshold would be 15% to 17%, where marine/brackish sediments are indicated by $C_{37:4}$ of less than 15% or lacustrine/isolated sediments of more than 17%.

4. Conclusions

[54] This is the first study to investigate alkenone distributions in such a diverse range of modern, shallow coastal environments. Accordingly, no previous study has reported such diversity of alkenone abundance and within-class distributions within a relatively small geographical area. Alkenones were present in varying concentrations in surface sediments of all the modern coastal basins

that had some tidal connection to the sea but were not detected in two freshwater (lacustrine) lochs.

[55] Distinct differences were observed in the alkenone patterns in the more open basins of Loch nan Ceall and Rumach tidal pond (IS 1, 2 and 3) compared with Craiglin lagoon (IS 4). This is characterized by increased values of %$C_{37:4}$ and lower relative abundances of $C_{37:2} + C_{37:3}$ and the C_{38} methyl alkenones in Craiglin. The reason for such a divergence in alkenone patterns over a relatively small area cannot be explained by the physiological response of *E. huxleyi* producers to changes in ambient water temperature. It must be due to a physiological response to other physiological stresses (such as salinity, or nutrient availability) by an *E. huxleyi* strain, or a product of different haptophyte populations.

[56] A logit regression analysis of all the sediment samples was employed to find which of the measured response variables could reliably characterize the sediment samples in terms of a marine/brackish or isolated/lacustrine depositional origin. The results suggested an good efficiency for %$C_{37:4}$ at predicting the depositional origin of the sediments, with %AA and alkenone concentrations also showing a strong relationship with the response variable. In particular, the results of this study suggest that the isolation contact basin sediments (transition from IS4 to IS5 in Figure 1) can be identified by a sharp change in alkenone concentrations accompanied by a change in %$C_{37:4}$ through a threshold value of ~15% to 17%. Other measures of biomarkers and organic geochemical parameters are less consistent in their response to sea level change and therefore have less utility for sea level studies. However, measurements of C_{org}/N and TOC may

provide other useful background information for a more complete environmental reconstruction.

Acknowledgments

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