IODP Proposal Cover Sheet

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Title:	A Shallow Drilling Campaign to Assess the Pleistocene Hydrogeology, Geomicrobiology, Nutrient Fluxes, and Fresh Water Resources of the Atlantic Continental Shelf, New England
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Abstract:

In many coastal settings around the world the distribution of freshwater within continental shelf sediments is far out of equilibrium with modern sea level conditions. One of the most remarkable examples of this can be found on the Atlantic continental shelf off New England where groundwater within shallow Pliocene-Pleistocene sand units over 100 km offshore Long Island are remarkably fresh (~ 3000 mg/l salinity). On Nantucket Island to the North, a 514 meter-deep borehole penetrating the entire Cretaceous–Tertiary sedimentary package showed considerable vertical variations in salinity with extremely fresh (< 1000 mg/l) waters in sand aquifers, higher salinity levels (between 30–70% seawater) in thick clays/silts and intermediate to low salinities in thin confining units, attesting to marked disequilibrium conditions because diffusion tends to eliminate such patterns. Pore fluids within Pleistocene to Upper Cretaceous sands beneath Nantucket Island were also found to be modestly over-pressured by about 4 m above the local water table.

We hypothesize that the rapid incursion of freshwater on the continental shelf in New England could have been caused by one or more of the following mechanisms: (1) Meteoric recharge during Pleistocene sea-level low-stands including vertical infiltration of freshwater associated with local flow cells that may have developed on the continental shelf during sea level low stands; (2) Sub-ice-sheet recharge during the last glacial maximum; (3) Recharge from pro-glacial lakes. We further hypothesize that the overpressures could be due to either:
(1) Pleistocene sediment loading; or (2) fluid-density differences associated with the emplacement of a thick fresh water lens overlying saltwater (analogous to excess pressures observed in gas legs of petroleum reservoirs).
We argue that these different recharge mechanisms can be distinguished using environmental isotope and noble gas data.

This work will extend our understanding of the current and past states of fluid composition, pressure and temperature in continental shelf environments. It will help better constrain rates, directions, and mechanisms of groundwater flow and chemical fluxes in continental shelf environments. *It will contribute to developing new tools for measuring freshwater resources in marine environments*. The apparent transient nature of continental shelf salinity patterns could have important implications for microbial processes and long-term fluxes of carbon and nitrogen and other nutrients to the global ocean.

Scientific Objectives:

We argue here that targeted drilling for the collection of hydrogeochemical, microbiological, isotopic, and noble gas samples, measurement of hydraulic properties and fluid pressures will permit us to unravel the origin of the offshore groundwaters and to quantify the role of continental shelves in global biogeochemical and climate cycles.

We propose to conduct a shallow (< 1000 mbsf) drilling campaign on the Atlantic continental shelf off Martha's Vineyard, Massachusetts to evaluate the above hypotheses and map the distribution of freshwater resources. We propose to drill six sites along a transect off Martha's Vineyard, MA. This transect takes advantage of existing borehole 6001 on Nantucket Island and ENW-50 on Martha's Vineyard. The sites were selected to obtain a suite of hydrogeochemical/microbiological samples across the freshwater-saltwater mixing zone. Based on paleohydrologic reconstructions by the PIs, the freshwater-saltwater mixing zone should be ~40 km offshore of Martha's Vineyard.

Our planned drilling campaign utilizing Rotosonic drilling in combination with cased/screened wells and packer systems for sampling should help us to overcome prior water/sediment sampling problems experienced on prior ODP and AMCOR drilling campaigns. Post cruise mathematical modeling including direct simulation of groundwater residence times and noble gas transport will be compared to observed pore fluid data to aid in our interpretation. The proposed work is highly interdisciplinary and would be the first to focus almost exclusively on the coupled hydrogeological/ biogeochemical/microbiological processes operating on the continental shelf.

Please describe below any non-standard measurements technology needed to achieve the proposed scientific objectives.

Collection of noble gas samples

Proposed Sites:

Site Name	Position	Water Depth (m)	Penetration (m)			Brief Site-specific Objectives
			Sed	Bsm	Total	
MV- 01	N 41:30 E 70:46	18	350		350	Characterize freshwater leg of transect
MV- 02	N 40:57 E 70:40	19	550		550	Characterize saltwater-freshwater transition zone
MV- 03B	N 40:39 E 70:33	48	650		650	Characterize saltwater-freshwater transition zone
MV- 04	N 40:32 E 70:20	59	750		750	Characterize saltwater-freshwater transition zone
MV- 05	N 40:22 E 70:15	80	775		775	Characterize saltwater-freshwater transition zone
MV- 06	N 40:12 E 70:10	109	800		800	Characterize saltwater- leg of transect

INTRODUCTION

Coastal zones are the terminus of continental aquifer systems[134,85]. In the past, hydrogeologists have regarded the offshore as the domain from which saltwater invades many onshore coastal aquifers in response to increasing groundwater withdrawals. This has changed recently with the growing attention paid to the phenomenon of submarine groundwater discharge[119] (SGD). While fluxes of fresh groundwater to oceans are probably volumetrically insignificant[136], interest in SGD has grown as hydrologists have recognized the importance of SGD as a conveyor of nutrients and pollutants to oceans and estuaries and their implications for marine ecology and biogeochemistry[69,111].

Recent assessments of brackish to freshwater in coastal aquifer systems in California[29], New Jersey[82], Suriname[38], and Sweden[133] indicate that tongues of fresh-to-brackish water extend tens to more than one hundred kilometers beyond the modern shore line[27]. These features are out of equilibrium with modern sea-level conditions[64,65,37,38,96] and appear to be the rule rather than the exception. One striking example is along the northeastern US Atlantic continental margin (Fig. 1) where scientific drilling campaigns during the 1970’s discovered unusually fresh pore fluids. Several boreholes located up to 100 km off the New Jersey and New England coasts (wells 6001, 6009, 6011, 6020; Fig. 1) had a salinity level below 3 ppt (parts per thousand) within Pleistocene, Pliocene, Miocene, and Upper Cretaceous sand units from 100-500 m below the seafloor[32, 63]. On Nantucket Island, MA, a 514 meter-deep borehole[32] (well 6001; Fig. 1) penetrating the entire Cretaceous–Tertiary sedimentary package showed considerable vertical variations in salinity with extremely fresh (< 1 ppt) waters in sandy aquifer units, higher salinity levels (between 30–70% seawater) in thick clays silts and intermediate to low salinities in thin confining units, attesting to marked disequilibrium conditions because diffusion tends to eliminate such patterns. The presence of an offshore freshwater lens in some coastal regions can be explained, in part, by present-day meteoric recharge to confined aquifers which outcrop on land (e.g. the Floridian Aquifer System). However, onshore hydraulic heads along the New Jersey to New York coast are too low to drive meteoric water very far offshore[65]. Moreover, around Martha’s Vineyard and Nantucket, confined aquifers crop out or subcrop below sea level which suggests that onshore, freshwater recharge cannot be happening. The fresh and brackish sub-seafloor pore waters that occur along the northeastern US Atlantic coast can be considered key examples of palaeo-groundwater emplaced during Pleistocene sea-level low stands which escaped salinization during Holocene sea-level rise (e.g.[48,82,64,96]). However, there is a dearth of information regarding the chemical composition, age, and distribution of these offshore palaeo-waters.

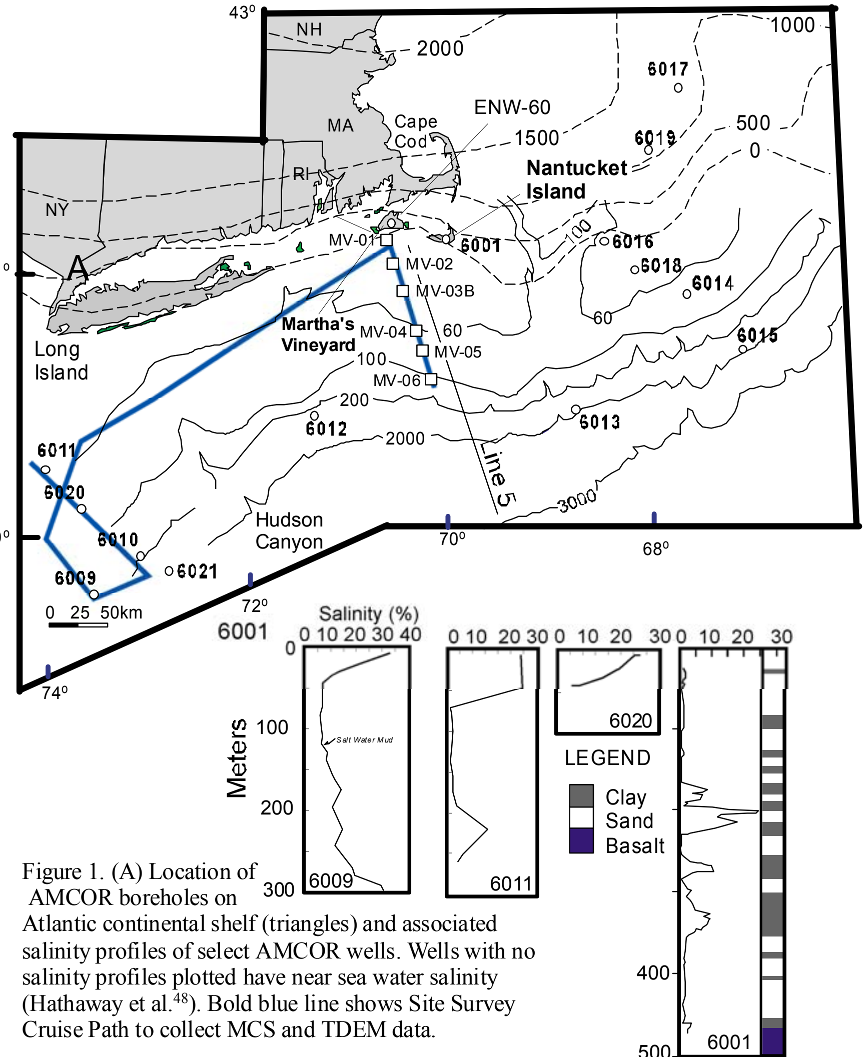

Figure 1. (A) Location of AMCOR boreholes on Atlantic continental shelf (triangles) and associated salinity profiles of select AMCOR wells. Wells with no salinity profiles plotted have near sea water salinity (Hathaway et al.[48]). Bold blue line shows Site Survey Cruise Path to collect MCS and TDEM data.

A number of mechanisms have been proposed to explain the emplacement of these freshwater plumes during glacial low-stand periods. Early studies focused on the shore-normal hydraulic gradient associated with primary topography of the continental shelf as the prime driving force for fresh water recharge during sea-level lowstands (Fig. 2A; e.g. [82,48]). More recently, Groen et al.[38]argued that local flow systems associated with secondary topography of the subaerially exposed and incised shelf are essential to emplace meteoric water far out onto the continental shelf (Fig. 2B). Person et al.[96] emphasized the role of sub-ice-sheet recharge (Fig. 2C), wheras Mulligan and Uchupi[86] suggested recharge from pro-glacial lakes (Fig. 2D). The mechanism proposed by

Groen[38] would be particularly viable if confining units are discontinuous as indicated by recent drilling off New Jersey. A problem that some of the above mechanisms face is that

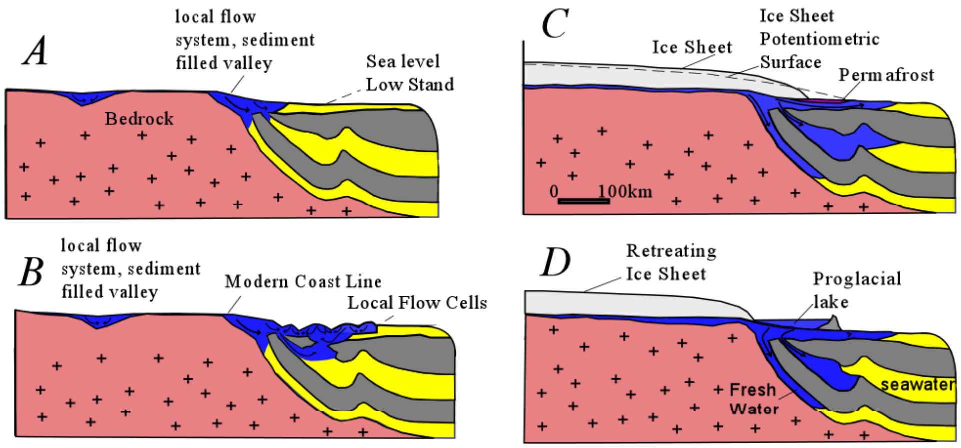

Figure 2. Conceptual models proposed to explain the incursion of fresh water into coastal plain sediments far out onto the Atlantic continental shelf in New England by (A) lateral incursion of freshwater during the Pleistocene sea-level low stands, (B) vertical infiltration of meteoric water induced by local flow cells, (C), Sub-ice-sheet recharge from the Laurentide ice sheet, (D) infiltration beneath pro-glacial lakes.

freshwater incursion far offshore is indicative of a permeable environment whereas observed (Nantucket, well 6001) and interpreted[24] (offshore New Jersey) excess fluid pressures suggest a low-permeability environment.

These different recharge mechanisms can be distinguished using environmental isotope (e.g. [35,81]) and noble gas (e.g. [126]) data. Based on ice sheet reconstructions[78] and changes in ice volume derived from marine isotopic records[18], we anticipate that glacial meltwater from the last glacial maximum should have an age between about 20,000 to 30,000 years. Meteoric recharge associated with the last sea level low stand should have ages less than 20,000 years. Recharge from pro-glacial lakes should have an age of about 18,000-15,000 years. Older groundwater from pre-Wisconsin sea-level lowstands may also be present. We propose to collect ^{81}Kr, ^{4}He, ^{14}C to constrain groundwater residence times on the Atlantic continental shelf porewaters.

Stable isotope analyses together with noble gas composition of groundwater from confined aquifers can also be used to distinguish groundwater that originates from basal melting of ice sheets, water that was recharged beneath pro-glacial lakes and water that originated from meteoric recharge on the sub-aerially exposed shelf (Table 1). The isotopic composition of oxygen and deuterium in precipitation are vary with temperature and distance from the ocean. The $\delta^{18}O$ of modern precipitation in New England is about -6 ‰. Groundwater $\delta^{18}O$ measured in Holocene waters on Nantucket aquifers range between -6 to -7 ‰. We expect that $\delta^{18}O$ of Laurentide ice sheet meltwater and proglacial lakes will be significantly depleted (< -20 ‰). This is based on analysis of the isotopic composition of proglacial lake clays[103,51], aquifers from the Williston basin[35] and isotopic signatures of Greenland and Antarctic ice cores (-45 to -35 ‰ $\delta^{18}O$) [55,8]. Therefore meteoric water is expected to be discriminated from subglacial recharge or recharge from proglacial lakes. Noble gas analyses should allow complete discrimination among the three water types (Table 1).

Table 1. How Proposed Recharge Mechanisms can be Identified Using Continental Shelf Environmental Isotope and Noble Gas Data

	^{14}C,^{4}He,^{81}Kr age (ka)	$\delta^{18}O$ ‰	$\delta^{2}H$ ‰	Ne (ccSTP/kg)	"Excess air" ΔNe %	Recharge Temperature reflects
Meteoric groundwater	<20 or interglacial	-6 to -10	-35 to -50	$2*10^{-5}$ to $5*10^{-5}$	30 to 100	Water table
Subglacial meltwater	20-30 or glacial	-45 to -35	< -350	$6*10^{-4}$ to $2*10^{-3}$	> 500	No unique solution
Proglacial lake/ surface water	20-30 or glacial	-45 to -20	< -350	$2*10^{-5}$	1 – 5	Lake surface

Noble gas contents in groundwater formed by direct recharge of precipitation is largely determined by dissolution equilibrium with the atmosphere, which is a function of the temperature at the water table. The temperature dependence has been widely used to infer noble-gas derived recharge temperatures (NRT) in paleoclimate applications for the tropics (e.g.[117,7,125]) and in mid-latitudes (e.g.[118,1]) on different continents. The concentrations of these gases in groundwater are determined mainly by solubility equilibrium with air in the unsaturated zone during infiltration. For our particular application, excess air (ΔNe) and Ne content should provide unique clues about the origin of the groundwater (Table 1). Admixture of excess air in groundwater that formed by infiltration of meteoric water through soils typically raises concentrations of Ne by 30-100% relative to solubility equilibrium. By contrast, excess air of lake water tends to be in the range of 1-5%[59,1]. Additionally, noble gas temperatures of the two water types may show distinct differences reflecting temperature conditions at the lake surface[59] and at the water table. Even more interestingly, noble gas concentrations of subglacial melt water are expected to be very distinct from both meteoric and surface water. In polar ice, noble gases are trapped in the form of air bubbles. In the firn layer (up to ~100 m thick), pore structure of the ice is connected. Below this layer air bubbles are closed off and preserved during downward transport. During basal melting of the ice under high ambient pressures, the air bubbles dissolve and the meltwater forced into the groundwater system without exposure to the atmosphere. Due to the absence of atmospheric disequilibrium dissolution, the excess air component of such groundwater should be extremely high (> 500%; J.P. Severinghaus, person. comm..). Consequently, in NRT analysis, progressive stripping of the excess air component would not converge to a unique solution for the component gases. Enrichment of the heavy species due to gravitational fractionation in the firn layer[19] is too small to affect such analyses. Recently, Vaikmäe et al.[126] reported anomalously high excess Ne in a confined aquifer system that was over-run by the FennoScandian ice sheet. These groundwaters also had light oxygen isotopic composition (-20 ‰ $\delta^{18}O$) believed to be derived from ice sheet meltwaters.

While most studies of chemical fluxes to the coastal regions have focused on modern, shallow near shore processes, the salinity data from New England and elsewhere in the world suggests that large-scale flushing of continental shelf sediments during the Pleistocene may have been associated with significant episodic fluxes of both nutrients (e.g., nitrogen [N], phosphorous [P]) and greenhouse gases (notably methane) to the oceans, biosphere and atmosphere. Through episodic flushing, the continental shelf may be an important contributor to global biogeochemical cycles and climate change. Currently, knowledge of the time-dependent nature and primary driving forces of these fluxes is lacking. Of particular importance in this respect are the rates of regeneration of the products of organic matter decomposition after a flushing event. Modern continental shelf environments frequently contain substantial amounts of methane[3,30,56,57] and other products of organic matter decomposition such as bicarbonate, ammonium and phosphate. High ammonium and phosphorous concentrations together with considerably higher N/P ratios (>>100 to ~1000) than the 'Redfield ratio' (N/P = 16) have also been observed in pore waters near the shelf break off New Jersey[5,74]. Discharge of this high N groundwater may drive N-limited coastal ecosystems towards P-limitation [111]. Virtual absence of methane in the upper 400 m of the New Jersey shelf (ODP Sites 1071, 1072;

AMCOR drillings 6009, 6010, 6011, 6020) suggests very low methane production rates. At the same time, ^{13}C isotopes of authigenic siderites and calcites indicate that methanogenesis did occur in the past[74]. The current low methane production rate is surprising because sulfate concentrations are sufficiently low and contents of sedimentary total organic carbon are high enough to favor methanogenesis[74]. Apparently, more complex biogeochemical processes affect production rates and should be unraveled to evaluate the role of continental shelves in biogeochemical cycles. Understanding the timing and rates of flushing as well as the source of fluids are critical to developing biogeochemical models that depend on the distribution and concentration of pore fluid nutrients.

Prior IODP drilling campaigns on the continental shelf have not been conducted with coupled hydrogeological/biogeochemical/microbiological research questions as the primary driving scientific objective. Available data are, therefore, far from sufficient to address the above issues. We argue for a dedicated IODP study involving targeted drilling and collection of hydrogeochemical, microbiological, isotopic, and noble gas samples, measurement of hydraulic properties and fluid pressures, and interpretation aided by direct simulation of multiple, natural hydrologic tracers will permit us to unravel the origin of the offshore groundwaters and to quantify the role of continental shelves in global biogeochemical and climate cycles.

STUDY AREA

Sediments of the Atlantic continental margin in New England have been studied extensively for their petroleum and mineral resources[94,48,79,100] and probed to assess water resources and chemical fluxes[62,82,112,101,10,95,74,96]. The hydraulic properties of these units have been inferred using in-situ measurements and model calibration. A series of boreholes were completed along the Atlantic continental shelf during the 1970's and 1980's as part of the Atlantic Continental Margins Coring (AMCOR) project[48], continental offshore stratigraphic test (COST) wells[109], and most recently by ODP[74] (Legs 150 and 174A). Sediments that accumulated on the Atlantic continental margin following the Mesozoic break-up of Africa and North America exceed 10 km in places. The deepest portion of the sedimentary wedge consists of relatively low-permeability carbonates and minor amounts of evaporites. Tertiary and Cretaceous unconsolidated sands extend tens of kilometers offshore before grading into finer-grained facies. The Tertiary and Cretaceous continental shelf deposits of New England are capped by a veneer of ~ 100- to 200-m thick marine sediments (silt and clay) and Pleistocene glacial tills and outwash sands. Multiple glacial and interglacial stages are documented on Nantucket Island and Martha's Vineyard[90]. Radiocarbon ages for glacial tills of the Atlantic continental shelf off New England indicate that the Laurentide Ice Sheet reached its maximum southern extent across Long Island and Nantucket about 21 ka before retreating onto the mainland by ~14 ka[124]. Reconstructed ice-sheet thickness is estimated to be 600-1000 meters near the toe of the glacier[21] (Fig. 1).

Several proglacial lakes formed following the last glacial maximum as the Laurentide Ice sheet retreated (Fig. 3). Seepage from proglacial lakes in Nantucket Sound, Cape Cod Bay, Block Island Sound, and Long Island Sound could have provided extensive freshwater recharge to confined aquifers of the continental shelf in New England[124]. When these proglacial lakes burst, rapid sediment discharge on the continental shelf would have changed the land surface morphology, induced rapid sediment loading, and perhaps induced infiltration of freshwater.

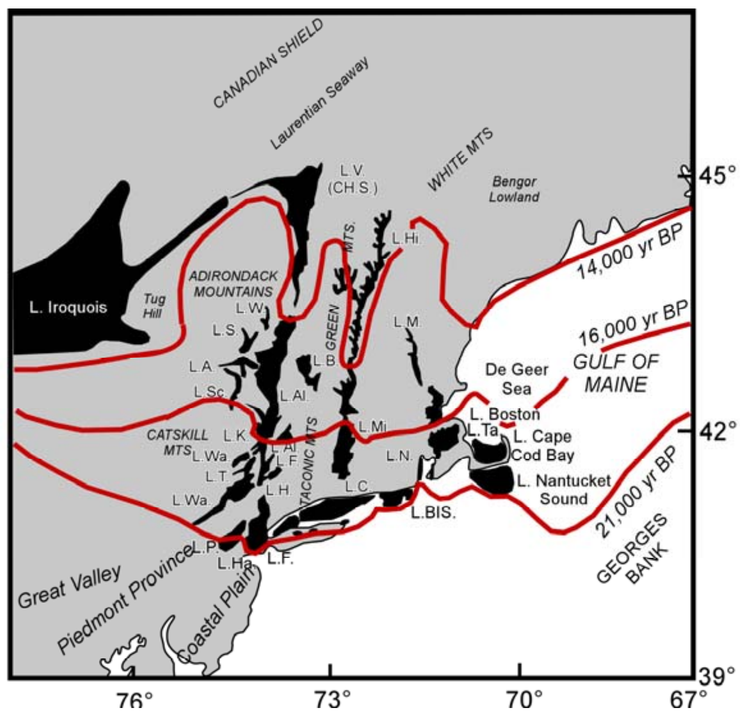

Figure 3. Distribution of proglacial lakes and position of maximum ice sheet extent during Late Quaternary on Atlantic continental shelf (after Uchupi et al.[124]).

A complex series of sedimentary sequences separated by well-developed unconformities have been recognized on the outer shelf off New Jersey and Long

Island[61,110] attesting to the marked changes in shelf morphology caused by fluvial and marine processes during regressions and transgressions of the sea during the Pleistocene. Seismic reflection profiles off New Jersey[11] provide detailed information about Pleistocene sequence stratigraphy and highlight extensive migration and incision of the palaeo Hudson River Valley. Lateral continuity of these aquifers and confining units is not fully known offshore and similar data are presently lacking for our proposed study area off Martha's Vineyard MA.

Inferred excess fluid pressures in Oligocene-Pleistocene sediments on the continental slope off New Jersey is interpreted to result from high sedimentation rates and focused fluid flow along permeable sand layers[24]. Interestingly, the hydraulic head in confined Tertiary and Cretaceous aquifer units on Nantucket Island (well 6001) is indeed elevated (i.e. has excess fluid pressure) above local water table by about 4 meters (Fig. 4). If similar, low-magnitude excess pressures had extended into the continental shelf during the late Pleistocene, they would have hampered or completely obstructed fresh-water recharge during those times. An alternative explanation for the excess heads at Nantucket is associated with fluid-density differences and the emplacement of a thick freshwater lens in a permeable system. This mechanism, analogous to pressure anomalies associated with gas reservoirs in petroleum basins[20], would have obstructed the emplacement of freshwater on the continental shelf during the Pleistocene. At present, insufficient offshore data exist for fluid pressures and salinity distribution to evaluate these observed/inferred excess pressures and to resolve between the conceptual models of fresh water emplacement.

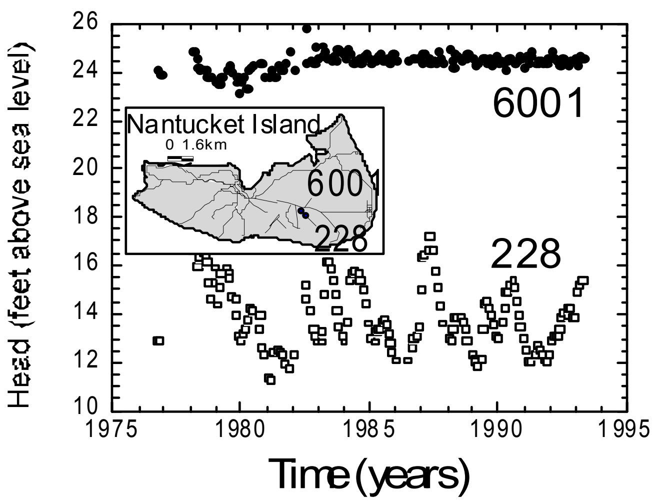

Figure 4. Head data comparing water table elevation and Cretaceous aquifers beneath Nantucket Island. The data indicated that the deep aquifers are anomalously pressured.

AIMS OF THE PROPOSED RESEARCH

We propose a shallow drilling campaign on the Atlantic continental shelf off Martha's Vineyard in waters between 18m to 109m depth using mission specific platforms (MSP). The primary objectives are to address: What is the distribution of freshwater, fluid pressures, and temperatures across the Atlantic continental shelf in New England? Do fluid pressures reflect the current fluid density distribution and modern sea-level or are overpressuring mechanisms (e.g., rapid sediment loading) involved? How old are the groundwaters and when where they emplaced? Was freshwater recharged by basal melting of large ice sheets, infiltration from large proglacial lakes, direct recharge from precipitation or a combination of these processes? If the latter, what is their distribution and can this distribution and the age patterns be unraveled through hydrogeological process models? What are the current concentrations and production rates of methane and nutrients (N/P) in shelf sediments? What controls them? What are the rates of decomposition of sedimentary organic matter and which redox processes/microbial communities are involved? Which factors determine the spatial distribution and activity of microbial communities in the shelf? What are the magnitudes of the long-term fluxes of methane and nutrients from the shelf due to periodic fluxing during the Pleistocene? Does the emplacement of ice sheet meltwaters in confined aquifers create a unique environment for methane generation observed in continental venues such as the Michigan/Illinois basins (e.g.[80])?

To address these questions, we propose a targeted drilling campaign which will: 1) Document the spatial distribution of sub-seafloor fresh and brackish groundwater in aquifers and confining units; 2) Determine the isotopic and noble gas composition of groundwaters of the continental shelf; 3) Reconstruct the history of groundwater flow during the Pleistocene using mathematical models and rock properties from drilling constraints; 4) Unravel the mechanism(s) by which freshwater was emplaced preserved; 5) Assess the microbiological ecosystem functioning in this shelf setting in relation to other fresh-salt transition zones (both continental and marine); and 6) Assess the role of microbiology in long-term methane and nutrient fluxes cycling the shelf to the ocean, atmosphere and biosphere through episodic hydraulic flushing of the shelf.

The work will be highly interdisciplinary, integrating "onshore" groundwater hydrological, hydrogeochemical, and micro-biological techniques and measurements, offshore sedimentological and paleo-oceanographic methods, novel offshore geophysical techniques and process-based hydrological and biogeochemical modeling at various scales. We have assembled a team of hydrogeologists (Kooi, Person, Groen, Dugan), biogeochemists (van Breukelen), isotope geochemists (Sauer), microbiologists (Röling), and sedimentologists (Litch, Kenter) to design a program that can address the questions.

COLLECTION OF NEW SITE SURVEY DATA

While numerous shallow seismic surveys have been conducted on the continental shelf off New England[61,123,28,32,42,60,53,114] these have been low resolution north of New Jersey. High-resolution multi-channel seismic (MCS) data off Martha's Vineyard are lacking (Fig. 5). Moreover, knowledge of the distribution of fresh/brackish offshore groundwaters is restricted to sparse borehole data (AMCOR, ODP Legs 150, 174A). We plan to resubmit a site survey proposal to the US NSF on August 15, 2005 to collect high-resolution MCS data and time-domain electromagnetic sounding data[31,33] (TDEM) off Martha's Vineyard during fall 2006 to resolve the distribution, thickness, depths and continuity of sandy aquifers and fine-grained confining units, to constrain the distribution of fresh/brackish waters, and to reconstruct the evolution of the Pleistocene shelf sediments that may have controlled fluid recharge and discharge.

TDEM data will be also collected during the summer of 2006 as part of the site survey proposal to map the distribution of sub-seafloor fresh and brackish groundwater. The TDEM data will be collected first along the New Jersey coast (Fig. 1) through several of the AMCOR wells and then offshore Martha's Vineyard. The TDEM data collected offshore Martha's Vineyard will provide important data for fine-tuning drilling plans and operations. The initial site survey proposal was rejected, in part, because the Groen has subsequently validated the method on the North Sea off Holland and we anticipate success in the upcoming submission to NSF Ocean Drilling Program.

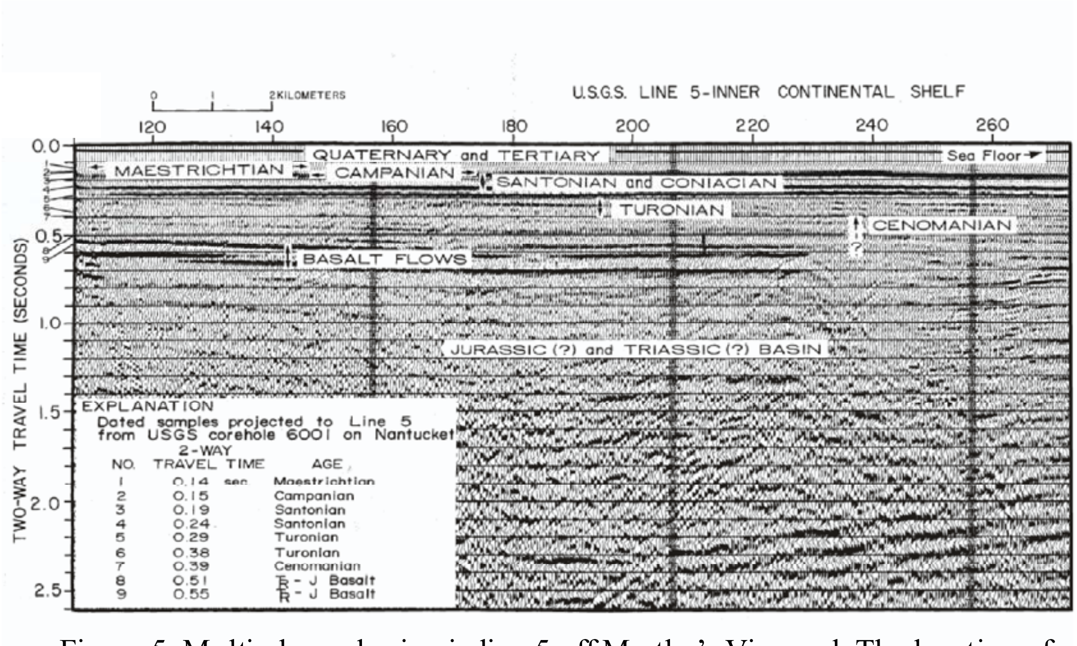

Figure 5. Multi-channel seismic line 5 off Martha's Vineyard. The location of line 5 is shown in Figure 1 (from Valentine[127]).

marine TDEM approach had not been adequately validated in a marine setting. PI

DRILLING & WELL COMPLETION

To address the proposed research questions, we propose to drill six sites (MV01-MV06, Fig. 6) off Martha's Vineyard, MA. This transect takes advantage of borehole 6001 on Nantucket Island[32] which is accessible to the PIs and borehole ENW-50 on Martha's Vineyard[45]. The sites were selected to obtain a suite of hydrogeochemical / microbiological samples across the freshwater-saltwater mixing zone. Based on paleohydrologic reconstructions[96] the freshwater-saltwater mixing zone should be ~40 km offshore of Martha's Vineyard.

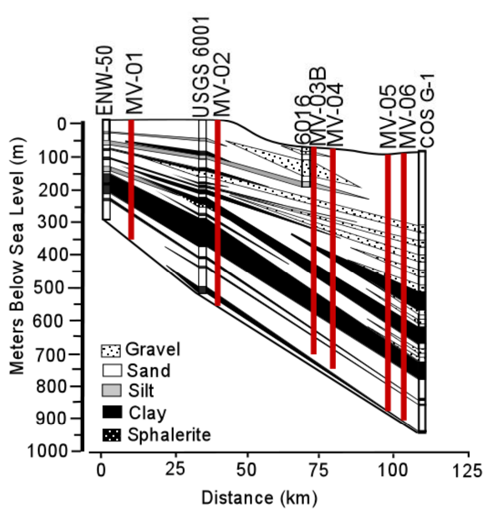

Figure 6. Proposed location and depth of boreholes and anticpated stratigrapy encountered off Martha's Vineyard.The location of the wells is also shown in Figure 1 (squares). The stratigraphy shown is based on available COST, and AMCOR wells.

We expect that the sand units from site MV01 will be entirely fresh and would have similar characteristics to wells 6001 and ENW-50. The groundwater should be Late to Middle Holocene in age with isotopic signature comparable to meteoric waters. This well will be used as the freshwater, marine end member. We would expect sites MV02-MV05 to contain Late to Middle Wisconsin aged groundwater with salinity ranging from 10,000-30,000 mg/l. If ice sheet meltwaters recharged the continental shelf, we would expect groundwaters of this composition within the sand horizons at these sites. We would expect of find vertical salinity patterns within confining unit pore waters consistent with vertical diffusion as observed in well 6001. We expect to obtain saltwater in both sands and clays at site MV-6. These wells defines the sea water end member of our transect.

Riserless drilling will need to be conducted using MSPs since water depths are too shallow for the JOIDES Resolution. Drilling will proceed from the seafloor to the base of the lower fresh-saline water transition zone which is expected to be found from 350 – 850 mbsf based on salinity data of the AMCOR wells[48]. Within this depth range, sediments will be primarily Holocene to Upper Cretaceous unconsolidated sands separated by silt/clay confining units. These horizons have been drilled by prior DSDP/ODP drilling campaigns[74] (DSDP Leg 95; ODP Legs 150/174A), on Nantucket Island[32] (UGSG 6001), and by COST wells (G-1 and G-2) north of Nantucket. A hydraulic sediment squeezer[75,76] was used to extract pore fluids samples from the AMCOR wells. Experience on ODP Leg 174A (Sites 1071, 1072) on the Atlantic continental shelf off New Jersey and AMCOR experience suggests that recovery of sand units may be an issue. There were many problems with both logging and coring these holes. Hathaway et al.[48] report caving and loss of logging tools. Folger et al. [32] report that sediment recovery was as low as 10 percent for well 6001. Best recovery was experienced in clay rich horizons. Coring methods included split spoon coring, driven barrel coring, and rotary coring[32]. More recently, Metzger et al.[84] report sediment recovery (13 % recovery) and logging problems on ODP Leg 174A at Sites 1071-1072. Logging-while-drilling (LWD) methods was successfully used at hole 1071G. Discussions with service companies and experienced shelf scientists, and review of the Shallow Water Drilling Program Planning Group report[52] confirm that technology exists to develop successful drilling and coring plans for sandy shelf units.

We plan to drill three holes per site (*A, B, C; Table 2*). We believe our proposed drilling strategy can overcome many of the limitations of drilling in sandy horizons on the continental shelf. We estimate that coring plus logging will take approximately 5-7 days per hole. We have allocated two days per site for completion of a targeted (spot) coring, collection of pristine biogeochemical and isotopic samples and hydrogeologic formation testing. Hole A will be a dedicated LWD well used to collect gamma ray/porosity/resistivity geophysical logs that are critical to the science and to identify target intervals for casing/coring/pump tests. Porosity logs and gamma ray logs will provide crucial information on lithology and hydraulic properties while resistivity data will be essential to construct continuous profiles of salinity and fluid density. The latter information is crucially important to assess to what extent fluid pressures are controlled by fluid density effects or whether additional overpressure generating mechanisms are at play. NMR (or CMR) logging is useful to obtain lithology-independent porosity and permeability estimates.

Table 2. Estimate of Drilling/Logging Time for Proposed wells

Well Name	***Distance (km)**	**Water Depth (m)**	**Well Depth (mbsl)**	**Transit Time (hr)**	**Drilling Time (hr)**	**Logging Time (hr)**	**Total Time (Days)**
MV 01	8	18.4	350	3	50	27	5.2
MV 02	29	18.6	550	3	68	32	6.2
MV 03B	61	45.8	650	2	76	34	6.6
MV 04	73	59.2	750	2	87	37	7.2
MV 05	90	80.3	775	1	93	37	7.4
MV 06	107	109	800	2	94	38	7.5

**Distance from Martha's Vineyard well ENW-50*

Hole *B* will be continuously cored either using APC to refusal (~300 mbsf) and XCB methods or alternative approaches designed for unconsolidated sand. Hole *B* will be cased as the drill advances to prevent bore hole collapse and 4" to 6" well screens will be set within Pleistocene to Cretaceous sand horizons for collection of hydrochemical samples and for aquifer testing. Porewater chemistry (salinity, major ions) and stable isotope data will be obtained from fine grained confining units using a hydraulic sediment squeezer technology[77]. We will also consider using a centrifation technique to measure the permeability of confining unit sediments[107].

We anticipate no problem with obtaining intact cores from confining units as indicated by previous drilling. The full suite of environmental isotope and noble gas data can be collected from the sand horizons using a packer system. Thus, even if sediment recovery from sand horizons is low, we will be able to obtain mission-critical fluid chemistry from the packer system.

An alternative to APC/ XCB coring, the methods used in previous studies, would be to use the Rotosonic method that is licensed to BortLongyear. The Rotosonic method can collect continuous core samples without the use of fluid or mud with or without rotation. Rotosonic or vibratory drilling uses high frequency mechanical vibration (50-150 Hz) to take continuous core samples, and to advance casing into the ground for well construction and other purposes. A sonic drill rig advances a three ten inch diameter (nominal) core barrel for sampling and can advance up to a twelve-inch diameter outer casing for the construction of standard and telescoped monitoring and recovery wells. When drilling, the core barrel is advanced ahead of the outer casing in ten to thirty foot increments, depending on the type of sediment. This drilling method is routinely used to collect continuous core to depths of 200m. PI Person completed a 100m scientific borehole on Nantucket Island in August, 2004 using this method. This hole was continuously cored and all but 1.5 meters of sediment was recovered from predominantly sandy deposits that are the onshore equivalents of the offshore sediments we propose to drill. For depth greater than 200m, conventional APC/XCB methods would need to be used. At depths greater than 200m, however, we would anticipate core recovery to improve using APC/ XCB methods. Once the Hole B is completed, well casing will be set with well screens set at sand intervals greater than 5 meters thick as documented by LWD and coring. Packer tests will be conducted to measure the hydraulic conductivity of the aquifers and to collect noble gas and environmental isotope samples. The Schlumberger/ Westbay Products MP38 or MP55 packer systems appear to be excellent choice for our application. These systems are routinely used to depths of 1200m within well casings ranging in size from 3.5 to 6.25 inches. The system includes measurement ports for collecting fluid samples and measuring fluid pressures during pump tests along multiple packed off intervals. Using our packer system, the wells will be pumped for a minimum of 30 minutes before sampling is begun in order to assure samples from the formation. Temperature, specific conductance, pH, turbidity, and dissolved-oxygen content will be monitored until readings stabilize (3 consecutive readings at 5-minute intervals that do not vary by more than 5%) before samples are collected. Samples will be collected through cleaned tubing attached to a port directly on the wellhead. Major anion samples and carbon-isotope samples will be filtered but do not need preservation. Water from sandy aquifer sections will be collected under pressure to prevent degassing which is essential for sampling noble gases and major gases. Groundwater sampling under continuous (either artesian or via pumping) flow is essential to obtain large volumes of water (up to 2000 L) to allow noble gas and ^{81}Kr analysis. We will use a gas stripping machine shipboard to extract ^{81}Kr from 2000 L of water for shipment and analysis. At a pumping rate of 38 liters per minutes (10 gpm) it will take less than an hour to collect one sample of ^{81}Kr analysis. All other noble gas and environmental isotope sampling would require far less time for sampling.

Hole *C* will be used for targeted sampling of pristine microbiological samples. Procedures and methods employed recently on the dedicated microbiology / hydrogeochemistry ODP Leg 201[23] will be used. It includes: (a) usage of the APC/XCB coring, (b) combined usage of cores for interstitial water analysis, geochemistry and microbiology, (c) procedures to avoid contamination by introduction of foreign microorganisms into the sediments[54]. Comparable procedures can also be implemented for operations that use alternative coring methods (e.g., Rotosonic).

HYDRAULIC TESTING

Formation Testing/Hydraulic Parameters and Pore Pressure: Assessment of hydraulic properties of sediments in the study area is essential to constrain both the large-scale and local-scale properties for palaeo-hydrological modeling and to assess the present hydraulic stability of fluid density stratification (upward increasing salinity and density). In situ formation testing to obtain estimates of horizontal and vertical permeability will be done within key horizons using dipole aquifer testing techniques[58, 137]. Pore pressures play a key role in fluid flow assessment and can only be evaluated properly in conjunction with accurate fluid density measurements. Measurements may either be done by probe tools (advance drilling), MDT tools (requiring time for pressure equilibration) or both. These measurements may be combined with temperature probing tools. In situ pressure of low permeability confining units will be measured directly with a probe penetration tool (e.g., piezoprobe) that has been successfully deployed within the Ocean Drilling Program (ODP Leg 204)[122] and in numerous Gulf of Mexico geotechnical studies (e.g.[92]). These measurements will document pressures and will provide estimates of permeability in the confining units (e.g. [26]). Each pressure measurement will take approximately 2 hours for set-up, deployment, measurement, and recovery of the tool. A total of 6 measurements (0.5 days total per well) will be completed. The permeability data will be used as inputs to flow models and the pressure measurements will be used to test these flow models. Diffusion coefficients of low-permeability units are crucial for transport modeling and will be obtained through radial diffusion cell measurements on clay cores[132, 102].

METHODS TO CONSTRAIN THE GROUNDWATER FLOW MODEL

Groundwater Age Dating: The age distribution of groundwater is essential information to constrain groundwater transport models of the continental shelf. We propose to apply three methods to determine the age of groundwater samples: ^{14}C, ^{4}He and ^{81}Kr (Table 3). Unfortunately, the ^{36}Cl method is expected to fail since groundwater chlorinity tends to exceed 75-150 mg/l[93]. The ^{14}C activity is expected to be strongly diluted with non-atmospheric carbon sources (carbonate minerals, organic matter) having a ^{14}C activity of zero (sediment age >> 60 kyr). In order to make the necessary corrections and calculate the true age we will apply a model such as NETPATH[99]. The ^{14}C method will provide strong evidence to distinguish groundwater from the last glacial event from older groundwater and together with other tracers (noble gases and $\delta^{18}O$, $\delta^{2}H$) will allow interpretation in more narrow age bounds. Also the buildup of ^{4}He in groundwater will help constrain the age of the continental shelf groundwater. Many studies have shown that increases in ^{4}He correlate with older groundwater (e.g.[120, 121]) and can be used (at least qualitatively) to date very old groundwaters[12, 13, 6]. The contents of U, Th and K in sediments will be measured on select core samples in order to calculate the in situ ^{4}He production rates and thereby the groundwater ages.

The concentration of the naturally occurring radionuclide ^{81}Kr produced by cosmic rays in the atmosphere and present in surface waters is expected to decrease in groundwater along a water flow line due to radioactive decay[115]. Of all proposed methods, the age interpretation of ^{81}Kr is most straightforward: 1) the atmospheric ratio $^{81}Kr/Kr$ was most likely constant over the past several hundred thousand years, 2) this input ratio into an aquifer does in particular not depend on the climatic conditions at the time of recharge, 3) subsurface production is small (Lehmann et al., 2003). The ratio will also not be affected as consequence of possible degassing during sampling. The only disadvantage of the method is the pumping of ~ 2000L of water, but can be solved using the proposed packer system (see before).

Table 3. Proposed Isotope Tracers that will be used to Date Groundwater

Isotope tracer	Half life (kyr)	Age range (kyr)	Complications of method
^{14}C	5.730	<50	Dilution by non-atmospheric carbon (without ^{14}C activity)
^{81}Kr	229	>50-1000	$2m^3$ of water needed for extraction
^{36}Cl	301	>40-3000	Dilution by stable oceanic chlorine
^{4}He	-	Unlimited	Correction for deep ^{4}He flux

Chemical Indicators of Salinization Mechanisms. Patterns of cation profiles (Ca, Mg, Na, K) with distance from the coast and with depth will be used to provide information on past and current processes of freshening and salinization in the shelf sediments (e.g.[38]). Cation-exchange results in characteristic chromatographic patterns during freshening/salinization[4]. The following water compositions (dominant cation and anion) are found in the direction of freshening: $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $NaHCO_3$. Salinization results in less pronounced chromatographic patterns but is indicated by $CaCl_2$ water types. Diffusive transport within and across aquitards can be constrained with conservative tracers Cl, Br, $\delta^{18}O$, $\delta^{2}H$ and $\delta^{37}Cl$ [22, 37, 38]. Modeling of vertical profiles of these tracers provide important information on the timing of onset of freshening and salinization. Modelling of multiple tracers (e.g., Cl and $\delta^{37}Cl$) allows simultaneous inversion for diffusion coefficients[41], which are necessary for numerical modeling of hydrogeochemistry.

MICROBIAL PROCESSES AND DISTRIBUTION OF MICROORGANISMS

The noble gas and environmental isotope sampling described above should elucidated what are the recharge mechanisms of fresh water and flushing rates on the continental shelf. Flushing of the shelf with fresh water may, by itself, have impacted the microbiology of the shelf sediments by changes in salinity, flushing of nutrients, and introduction of oxygen[80,81]. We propose to obtain a broad image of the microbiology of the shelf sediments by determining the abundance, activity and distribution of various types of microorganisms and how these are related the special hydrogeochemical characteristics (e.g types and concentrations of redox species, the bioavailability of organic matter, and salinity) of these fresh water containing shelfs. We will use both culturing-independent and culture-based methods. Furthermore, we want to determine the rates of microbial reactions (resulting in production of nutrients and greenhouse gases) and understand the factors which control these rates in order to address the question whether episodic flushing of the continental shelfs on geological time scales has resulted in massive releases of greenhouse gases and nutrients to the oceans and what its effect may have been to global biogeochemical cycles and climate change. We will determine the rates of microbial reactions using two approaches: 1) sediment incubations[23], 2) determination of groundwater/interstitual water (isotope) chemistry (redox species, nutrients) in combination with reactive transport modeling.

We will study the presence and activity of methanogens, sulfate-reducers and iron-reducers. Oxygen consumption and nitrate reduction are not expected to play a role in the biogeochemistry of the fresh/brackish water plume, since oxygen and nitrate are usually depleted in the first few meters below the sea floor (M. J. Malone, pers. comm.). Anaerobic ammonium oxidation (ANAMMOX), which requires nitrite or nitrate, is therefore also not considered of importance here. However, anaerobic methane oxidation (AMO) with sulfate may be of importance locally.

Microbiological analysis: Cultivation-independent nucleic-acid based analysis will be applied to gain rapid and detailed insight in microbial community structure and activities[49]. The Polymerase Chain Reaction (PCR) will play a central role in the approach as this technique allows the specific amplification of minute amounts of nucleic acid information, which is of high importance for low-biomass environments such as the deep subsurface. DNA-based analysis will provide information on the presence of certain types of microorganisms. RNA-based analysis provide insight on current activity, but the isolation of RNA is more challenging. Rapid insight in microbial diversity will be obtained by 16S rDNA-based Denaturing Gradient Gel Electrophoresis[49]. These analyses will be followed up by detailed phylogenetic analysis of 16S rRNA genes. In order to establish relationships between different locations, as well as between community structure and hydrochemical parameters, detailed numerical analysis will be performed[104, 105].

16S rRNA gene based analysis provides insight in whole communities, as all microorganisms possess this gene as its product is essential for protein synthesis. However, 16S rRNA information often does not inform on the functional role of the microorganism possessing it. Functional genes provide such information, as they encode specific functions, such as enzymes involved in sulfate reduction or methanogenesis. Specific groups of electron-accepting microorganisms will be addressed by combining group-specific16S rRNA gene amplification with the amplification of functional genes. Methanogens will be detected based on amplification of 16S rRNA gene and the gene encoding methyl coenzyme-M reductase (*mcr*)[44,73]. Molecular diversity and activity of sulfate reducing bacteria will be determined based on amplified dissimilatory (bi)sulfite reductase (*bsr*) gene sequences and reverse transcription of mRNA templates[72,88]. For the detection of specific groups of iron-reducing microorganisms, sets of primers are available that target important groups of marine iron-reducers (e.g. *Shewanella*, *Geobacteraceae*) [97,113]. If certain types of electron accepting microorganisms are present, their numbers and levels of gene-expression will be determined by quantitative approaches based on real-time PCR and most probable number PCR[49]. Molecular diversity in a certain functional group will be examined by terminal restriction length fragment polymorphism of amplified products[71].

Reverse methanogenesis by *Archaea* is considered important in anaerobic methane oxidation[16]. Several groups of anaerobe methane oxidisers have been identified, based on 16S rRNA analysis[91]. We will determine the presence of these groups using a combination of *Archaea*-specific PCR, followed by probing with group-specific oligonucleotides[91]. If the *Archaea* are present, PCR fragments will be cloned and sequenced to confirm the results. In order to detect the potential for aerobic methane oxidation, methane monooxygenase genes (e.g.[50]) will be measured. With culturing and sediment incubations[23] we will complement the cultivation-independent analysis and the hydrogeochemical measurements. Focus will be on redox processes (methanogenesis, sulfate-reduction, iron-reduction).

Hydrochemical, isotope geochemical and gas measurements: Microbiological data will be combined with hydrochemistry and isotope geochemistry to improve insight in the redox chemistry. Concentrations of dissolved organic carbon (DOC), acetate, formate, redox species, pH, alkalinity, nutrients, and major ions will be determined on interstitial water and all groundwater samples (see Table 4). Procedures from ODP Leg 201 will be used. The hydrogen gas concentration and possibly the concentrations of volatile fatty acids (VFAs: acetate, formate) give information on the governing redox processes, e.g., iron-reduction, sulfate-reduction or methanogenesis[17], and will be related to the microbiological data. Hydrogen gas concentrations will be determined via 1) the "bubble strip" method, continuous groundwater flow and re-equilibration in a gas sampling bulb[15] and 2) via sediment incubations (using procedure from ODP Leg 201). Measurements will done shipboard.

Stable isotope analysis on groundwater samples will aid in establishing: 1) the pathway of methane production ($\delta^{13}C$-CH_4 together with δ^2H-CH_4: acetate fermentation, CO_2-reduction or thermogenic[43]), 2) the occurrence of anaerobic methane oxidation (AMO; $\delta^{13}C$-DIC decreasing below -20 ‰, $\delta^{13}C$-CH_4 considerably higher than methane away from AMO zone), 3) the occurrence of sulfate-reduction (increase in $\delta^{34}S$-SO_4, $\delta^{18}O$-SO_4), and 4) the overall reaction network ($\delta^{13}C$ –DIC; decreasing to -20 ‰, sulfate-/iron-reduction; increasing up to + 10‰, methanogenesis; decreasing below -20‰, AMO at SO_4/CH_4 interface).

Gases measured by the headspace technique are only retained by the sediment after outgassing has taken place during core retrieval to the surface. Accurate gas concentrations will therefore be determined on groundwater samples obtained at overpressure exceeding in-situ gas pressure. A venturi valve will be used to maintain high fluid pressures and prevent degassing. The major gases CH_4, O_2, N_2 and its isotopes, Ar, and CO_2, and noble gases will be measured.

Table 4. Summary of Sampling and Analysis Methods

	Sampling method	Sample size	Analysis
Interstitial water (IW) composition*1	Both coring (APS/XCB/ Roto) and groundwater	Pore water extraction on 5-30 cm long whole-round sediment intervals	S, P
Geochemistry	Coring (APS/XCB/Roto)	On IW extracted sediment	S, P
Microbiology	Coring (APS/XCB/Roto) and groundwater	Samples of ~200 g adjacent to IW samples	S, P
Groundwater composition*1	packer system		S, P
Dissolved gases*2	Groundwater	2x1L in stainless steel cylinder	P
Nobles gases*3	Groundwater	2x40 mL in Cu tube	P
Hydrogen gas	Groundwater / Sediment incubations.	"bubble strip" method	Directly: GC
Stable isotopes of redox species*4	Groundwater	~2L total in HDPE/glass bottles	P
^{14}C-DIC	Groundwater/IW	~ 8-20 mL (1 mg C required)	P: AMS*5
^{81}Kr	Groundwater	~2000 L, extraction shipboard	P: ATTA*6

*1 **(Interstitial) water composition**: salinity, pH, alkalinity, Na, K, Mg, Ca, Cl, Br, F, I, NO_3, NO_2, Mn, Fe, SO_4, H_2S, NH_4, HPO_4, H_4SiO_4, Sr, Ba, B, Li, Cu, Mb, Ni, V, Zn, As, dissolved organic carbon (DOC), formate, acetate, $\delta^{18}O$, $\delta^{2}H$, $\delta^{37}Cl$, ^{13}C-DIC, methane, $^{87}Sr/^{86}Sr$.
*2 **Dissolved gases:** CH_4, O_2, N_2, CO_2, Ar, $^{15}N/^{14}N$.
*3 **Noble gases**: He, Ne, Ar, Kr, Xe and ^{4}He, $^{3}He/^{4}He$ ratio, ^{40}Ar, $^{40}Ar/^{36}Ar$ ratio.
*4 **Stable (redox) isotopes:** $\delta^{13}C$-DIC (> 5 mg HCO_3 [~50mL]), $\delta^{13}C$-CH_4 & $\delta^{2}H$-CH_4 [~1L], $\delta^{34}S$-SO_4 & $\delta^{18}O$-SO_4 [20mL (10mM SO_4) to 1L (0.1mM SO_4)], $\delta^{15}N$-NH_4 [~1L].
*5 **AMS:** Accelerator Mass Spectrometry
*6 **ATTA:** Atom Trap Trace Analysis[115]
P – Post Cruise, S – Shipboard, Roto – Rotosonic Drilling Method

Geochemical Measurements: Microbiological and hydrochemical data will also be combined with geochemistry data in order to understand the distribution and activity of microorganisms. The following geochemical measurements will be performed on sediment samples: total element analysis via X-ray fluorescence (XRF) and ICP-MS/optical ICP on HF extracts (also U, Th, K to determine in situ production of ^{4}He, ^{40}Ar), total carbon/sulfur/nitrogen on CNS elemental analyzer, total inorganic carbon, content of manganese- and iron-oxyhydroxides (using chemical extractions), thermogravimetry (TGA)/differential thermal analysis (to quantify the content of siderite, calcite and dolomite), the contents of opaline silica, glauconite sands, barite, iron sulfur minerals (using chemical extractions), X-ray diffraction (XRD), rock-eval pyrolosis and pyrolysis-gas chromotography/mass spectrometry to characterize the chemical composition of sedimentary organic matter[47], micro-oxymax experiments (Columbus Instruments, OH) to determine the redox reactivity of sediments[46], scanning electron microscopy, $\delta^{13}C$, $\delta^{18}O$, and $^{87}Sr/^{86}Sr$ of authigenic carbonate minerals for determining palaeo-biogeochemical conditions[74].

POST-CRUISE MODELING

Results of the drilling, isotope, and biogeochemical analyses are expected to provide a comprehensive set of constraints that will lead to refined, or perhaps even considerably altered conceptual picture of the origin of the offshore fresh and brackish waters. Numerical modeling will be undertaken to provide a process-based framework for integration of the geological, geochemical, and microbiological constraints that allows testing of conceptual ideas. Local/regional scale variable-density flow modeling will be done to infer present flow directions and rates from pressure and salinity (density) data. By gaining measurements of Pleistocene sedimentation rates and the distribution of freshwater, this analysis should be able to resolve the causes of observed anomalous pressures. Cross-sectional models (2D) of the Atlantic continental shelf paleohydrogeology[82,101,96] (e.g. Fig. 7) did not represent the effects of local flow cells associated with the topographic relief on the continental shelf during sea level low stands. PIs Person and Kooi will construct a regional three-dimensional hydrologic, thermal, and solute transport model of New England's continental shelf. Three-dimensional representation of flow and transport processes on the Atlantic continental shelf is also warranted because of the irregular geometry of the Laurentide Ice Sheet and the presence of submarine canyons on the continental shelf which would produce a three-dimensional groundwater flow field with both local and regional flow systems on New England's continental shelf (Fig. 1). PI Person currently has an NSF grant to develop three-dimensional models of variable-density groundwater flow and the New England Continental shelf (NSF 0337634). These models will need to be refined using drilling results. These models will incorporate direct simulation of groundwater residence time[34] so direct comparisons can be made between observed and model ages. Because most of

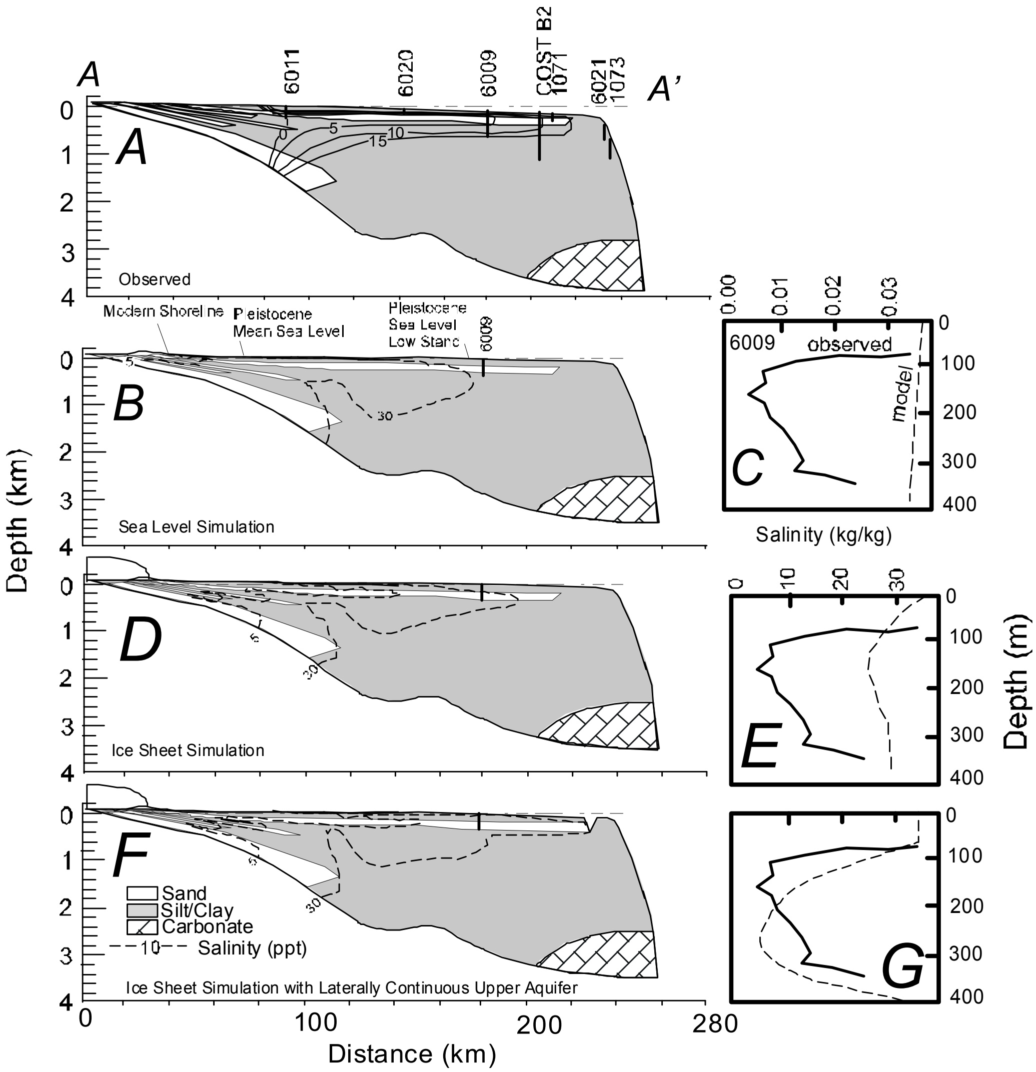

Figure 7. Observed (A) and simulated distribution of salt and freshwater on Atlantic continental shelf off Long Island due to sea level fluctuations (B) and sub- ice-sheet recharge (D, F). Simulated and observed (well 6009) were compared. Best agreement between observed and computed salinity occurred for the case where the Pliocene-Miocene aquifer outcropped along a submarine canyon (F-G). The observed salinity cross section was estimated using available borehole data from the Atlantic continental shelf off New Jersey and Long Island. The position of the cross section is shown in Figure 1.

the glacial landscape is buried under Holocene sediments, it will be important to reconstruct the buried topography by seismic, acoustic and bathymetric surveys. This will also be important for determining the sediment loading rates during the Pleistocene. In addition to regional models, PI Kooi will develop more detailed models of conditions and processes at the local scale including mixing by free convection[66]. Large-scale models will constrain regional processes and provide realistic boundary conditions for the smaller-scale models. Using results from the regional scale variable-density solute transport model, reactive transport modeling will also be conducted using the PHWAT code (http://www.see.ed.ac.uk/~xmao/phwat.htm) to enable simulation of the pore water hydrochemical, sediment geochemical and isotope geochemical profiles across the brackish/fresh water plume. Simulation of the ^{13}C of porewaters and sediments will act as additional constraint for the reaction network. Processes included will be cation-exchange induced by freshening/salinization, degradation of sedimentary organic matter coupled to the various redox processes, anaerobic methane oxidation, precipitation and/or dissolution of diagenetic minerals such as siderite and pyrite, and potential degassing of methane. The rates for iron-reduction, sulfate-reduction, and methanogenesis will be obtained via calibration of the model on both hydrogeochemical profiles and groundwater age tracers. This approach is believed best to accurately determine rates of sedimentary organic matter decomposition in low reactive aquifer systems[87], since radiotracer residence time experiments may overestimate rates of TOC degradation by three to six orders of magnitude[98]. Model scenarios will also be run to evaluate the biogeochemical dynamics of the continental shelf sediments during sea level fluctuations and associated flooding with sea water and flushing with fresh water. PI Van Breukelen has expertise in biogeochemical transport modeling[128,130,131,129]. Finally, results of the biogeochemical modeling will be up-scaled and linked to the large-scale flow and transport modeling to provide a quantitative framework for assessment of the long-term flux of methane and N/P nutrients to the atmosphere, biosphere and the ocean.

RELEVANCE TO IODP

The proposed drilling is consistent with many of the goals of the IODP Hydrogeology Program Planning Group (HGPPG) and the Deep Biosphere and Subseafloor Ocean theme of the IODP science plan. The proposal addresses explicitly a number of key scientific questions from those reports, notably HGPPG p. II:

- What was the past state of fluid systems (palaeohydrology)?
- How did the palaeohydrologic system transport mass and heat?
- What are the magnitude and distribution of porosity and permeability?

Moreover, the proposed research meets several HGPPG recommendations:

p.V: Conduction of dedicated hydrogeology legs in coastal zones examining "the origin and dynamics of submarine pore water" and "processes that operate at continent-ocean boundaries". Several aims of the proposal are explicitly mentioned: "How far offshore do continental flow systems extend and how do such systems influence water chemistry in marine sediments? How does the distribution of fresh and brackish water offshore relate to past sea level changes? What is the relative importance of compaction driven flow? To answer these questions, it is essential to invest a major effort in obtaining data from coast to shelf at depths less than one kilometer, which will require shallow water drilling capabilities. The type of data needed are pore pressures, fluid density profiles, fluxes at the sea floor, temperature profiles, permeability measurements from core to formation scales, and geomorphology and biota distributions." *p. VIII:* "Pre-cruise hydrogeologic modeling should be carried out before a drilling leg because the modeling can give scientists a conceptual understanding of the hydrogeological system. This can be of help in formulating hypotheses and defining investigative strategies when only limited data are available". "Post-cruise modeling is done to synthesize and demonstrate the state of knowledge following a drilling leg". The proposal does not directly fit one of the eight initiatives of the IODP Science Plan but, rather, takes advantage of the provision in the Implementation Plan (p. 71) to "pursue new opportunities and approaches as they emerge". It addresses elements of the "Deep Biosphere and Subseafloor Ocean" theme such as "The hydrogeological regime of passive rifted margins" (p. 24).

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