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## **Final Report**

Research Project

**Imaging and elemental analyses of the growing edge of shells from a  
commercially important bay scallop shell (*Argopecten irradians*)  
using a multi-method approach**

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# Proposal

## Introduction

Over the past years a considerable amount of research has been done using historical records of trace elements in bivalve shells. Trace elemental concentrations of bivalve shells have been used to reconstruct environment life histories, making them useful indicators of climate, pollution and ecosystem changes [1-4]. During the process of calcification, minor and trace elements existing in the surrounding environment can precipitate in the calcium carbonate matrix of the shell [5-10]. Previous studies suggest that incorporation of elements in shell layers were related to various environmental characteristics [11-13]. For instance, in a range of bivalve species, the ratios of Mg, Sr and Ba to Ca are considered as environmental indicators reflecting temperature, salinity and productivity respectively [14, 15]. Chemical and physical characteristics of the water also influence the incorporation of some elements in bivalve shells thereby elemental record of these shells can be used as a proxy for changes in seawater chemistry [16, 17]. Very recently elemental fingerprinting (element/Ca ratios) has been used to resolve the location of essential habitats for a special type of shell [18]. Despite of the research that has been done on shell analysis for half a century, most of the trace elemental variations are still not well understood and trace elemental proxies are far from being routinely applicable.

Up to now a variety of techniques to detect minor and trace elements in the shells are applied. Analytical techniques such as graphite furnace atomic absorption spectrometry (GF-AAS) or inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma

mass spectrometry (ICP-MS) using liquid sample introduction do not provide sufficient spatial information about the distribution and gradients of certain elements of interest in the samples. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is one of the newer techniques and is becoming widely employed for geological samples and biogenic carbonate [5, 14, 19]. Laser ablation micro-sampling is enabling analysis of a large number of elements, allows rapid analysis of solid samples, offers high spatial resolution, very little sample preparation and reduced possibilities for sample contamination. Considering sample preparation and analysis, it is a fast method compared to liquid ICP-MS [5, 8, 19, 20]. Although LA-ICP-MS is a powerful method to reveal in element concentration, obtaining accurate quantitative data from biogenic carbonate can be problematic. Due to the lack of suitable calibration standards, determination of trace elements in calcium-rich materials by LA-ICP-MS is not an easy task and is always very challenging.

## **Objectives**

The goal of this project is to enhance our understanding of the elemental chemistry of adult and juvenile Nantucket bay scallop shells (*Argopecten irradians*) which will pave the way for the application of trace elemental proxies to reconstruct environmental and climatic changes. The aims of this project are

- Developing a new LA-ICP-MS method for **determination of minor and trace elements in the growing edge of shells** from a commercially important bay scallop shell (*A. irradians*).
- **Assessing the accuracy** at LA-ICP-MS analyses of trace elements ratios in –shells by using synthetic calcium carbonate pellets

(MACS-1 and MACS-3) which recently produced by the United States Geological Survey (USGS).

- **Verifying the results** of LA-ICP-MS using wet chemical methods (ICP-OES and GF-AAS).
- Applying of SEM for imaging of shells to **investigate their elemental distribution and morphology**.
- **Determination of trace elements within culture water** by means of ICP-MS in order to investigate the influence of water on the incorporation of elements into the shells during the process of calcification.

Moreover, the work will uniquely include **mineralogical evaluation** of the growing edge of shells from organisms grown under pCO<sub>2</sub> conditions.

### **Importance of the Study Area**

We will focus on specimens from Nantucket Harbor due to its significant commercially fished bay scallop (*A. irradians*) population. In Massachusetts (MA), commercial populations of *A. irradians* occur in the waters of Cape Cod and the Islands. Landings of *A. irradians* in MA have declined precipitously over the past two decades from a mean of 399 metric tons (\$1.4M) in the 1980's to a mean of 47 metric tons (\$1.1M) from 2003 to 2010. As landings have declined, the market value of the MA *A. irradians* has increased. The market price and import pressure (especially from China) have led to a significant increase in coastal aquaculture research centered on the *A. irradians*.

### **Materials and Methods**

#### **1) Sampling and Sampling Sites**

Site locations and number of scallops retrieved follow the sampling protocols of the Nantucket Shellfish Management Plan (<http://www.nantucketharborplan.com/>). In order to gain representative data 30 sites of Nantucket Harbor will be evaluated from mid-August to mid-September 2013 for the presence/absence of *A. irradians*. Water sampling will occur between 9 a.m. and 11 a.m. to reduce the number of factors influencing pH, which is known to change over a daily cycle. In situ measurements of bottom water quality (e.g. pH and salinity) will be made at the time of collection.

## **2) Analytical Procedure**

### **2.1) Sample preparation**

Separation of soft tissues from the shells will be done using a Teflon coated spatula. The shells will be then cleaned by initially scrubbing off loosely attached particles in 18.2 M-Ohm water with a non-metal brush [21] and rinsing in glacial acetic acid for 60 seconds, followed by 2 consecutive 1-minute soaks in 18.2-M Ohm water. Samples will be allowed to dry overnight under laminar airflow at room temperature to be ready for the analytical measurements.

### **2.2) LA-ICP-MS**

Solid shell material will be analyzed for determination of major and trace elements using LA-ICP-MS. The device is an ICP-MS (Perkin Elmer ELAN DRC II) coupled with a laser ablation system (213 nm Nd:YAG; Cetac Technologies). During laser ablation, Helium gas will be used as sample gas in the ablation cell and Argon will be subsequently added to the gas flow.  $^{43}\text{Ca}$  will be used as the internal standard and FEBS-1 (otolith) will be an external standard. USGS carbonate standard reference

materials (MACS-1 and MACS-3) will be measured to monitor accuracy and instrumental drift. After monitoring the various elements, signal processing will be performed using GeoPro2010 Software (Cetac Technologies).

### **2.3) ICP-OES and GF-AAS**

In order to evaluate the accuracy of the LA-ICP-MS results, complementary analysis of some of the samples by solution analysis will be considered. After grinding the samples, a microwave-assisted sample dissolution (Anton Paar Multiwave 3000) using hydrochloric and nitric acid will be performed. Analysis by ICP-OES (Spectro Ciros Vision EOP) and GF-AAS (Analytik Jena Contr AA 700) will provide the average element concentration in the shell.

### **2.4) Mineralogy**

From plane polarized light digital photographs and from scanning electron micrographs, a number of shell morphologic features will be measured including length (distance between the anterior and posterior edge of the shells), width (longest distance between the dorsal and ventral edges perpendicular to the length of the shells), perimeter (to be traced automatically using edge recognition, ImagePro Plus), area, circularity ( $4\pi \times \text{area}/\text{perimeter}^2$ ), the circularity index ( $\text{perimeter}^2/\text{area}$ ,  $16=\text{square}$ ,  $4\pi=\text{circle}$ ), and, where possible, volume (estimated from mass and density of the dominant mineral phase). We will also describe the morphological characteristics such as crystallization front geometry, umbo position, width and major/minor growth line position. Changes in crystal habit (SEM images) will be scored (1=orthorhombic–aragonite, 2=prismatic–aragonite, 3=hexagonal–vaterite) and relative abundances

will also be noted as will changes in growth along the c-axis, which will indicate a shift from aragonite to vaterite. For polymorph comparisons (SEM images), shells will be scored: (1) completely aragonite, (2) vaterite  $\leq 33\%$ , (3) vaterite 33% to 66% and (4)  $\geq 66\%$  vaterite.

### **Application of Work**

Determination of trace elements in different types of shells has shown many advantages for other disciplines outside of geochemistry. For instance, environmental managers are using trace elements content as bio-indicators of metal contamination in coastal habitats. Population biologists also use trace elements content as natural tags to track dispersal. We believe that results of this work can be applied for different purposes such as: (i) recorder of habitat use, (ii) indicators of pollution, climate variation and ecosystem changes, (iii) developing proxies of environmental conditions and geochemical proxies and (iv) a proxy record for changes in seawater chemistry.

### **Added Value of Collaboration**

This proposed project is an interdisciplinary project and involves the combining of two disciplines in USA and Austria into one activity. In this project the group of Prof. Günther Knapp/ Dr. Helmar Wiltsche in the Analytical Chemistry Department, Graz University of Technology (TU Graz), Austria and the group of Prof. Robyn Hannigan in the Department of Environmental, Earth, and Ocean Sciences, University of Massachusetts Boston, USA will use their approaches and modify them to be better suited to the problem of shell analysis.

This collaboration will be beneficial for both universities to work on an important topic and will open windows for the future collaboration



between TU Graz and University of Massachusetts Boston. The project requires an optimum combination of human resources, expertise and research ideas. These qualities can be found within these two groups to achieve the ambitious goal of this research project. At TU Graz, there is no LA-ICP-MS for analysis of solid samples therefore this collaboration will be a great opportunity for trace element evaluation of a commercially important organism using the state of the art LA-ICP-MS that has been developed in Prof. Hannigan's group at University of Massachusetts Boston. The synergy of the complementary expertise covers the whole field of the planned research activities.

This work will be a part of my doctoral thesis. Besides the mentioned advantages of this collaboration, I can develop my knowledge, competence and skills in newer analytical techniques like LA-ICP-MS. I can transfer my practical knowledge about this powerful technique to my colleagues and also the students at TU Graz, whom I supervise in Chemistry lab courses.

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# Final Report

## Introduction

Through the past decade, the number of bivalve shells studies has intensely increased and particular volumes have been published. Began from the studies on corals this explanation was recently distinguished as “the investigation of physical and chemical changes in tough tissues of organisms and the time-based environment that they formed” in order to “realize organismal life history behaviors as well as to rebuild histories of environmental and climatic change through space and time” [1-6].

Nevertheless, consistent proxies of past environmental conditions other than  $\delta^{18}\text{O}$  values do still not exist. High-potential applicants, which are normally used in coral, are various elements to calcium ratios [2-10]. Changes in trace elements of bivalve shells delivering unreliable results and are very possible affected by non-environmental effects such as kinetic effects, biological properties and other properties.

Marine bivalve shells, like the bay scallop (*Argopecten irradians*), have the capability to portable numerous distances from their natal environment. However, in some cases, larvae may be engaged in a clear,

local environment [10-15]. Elemental fingerprinting of shells has been applied to rebuild environmental life histories (changeability in environmental contacts that lead to different elemental signatures from various locations) of organisms [16-19] and classify vital habitats [20,21]. Vital environment, in this report, is expressed as a mixture of physical structure, accessibility of food which creates the area best environment for *A. irradians* [23-27]. If there is enough change in elemental signatures in shells between positions, and enough constancy in water chemistry inside sites, then it is possible to with hindsight determine the place in which the organism lived before to capture. As these elemental signatures are rare to the environment and related to individuals, they can work as a natural tag for tracking movement forms, eliminating the important for artificial tagging [28-35]. Reviewing connection of environments in populations that are geographically limited is problematic given possibly low difference in water chemistry between sites that may inhibit identification of rare fingerprints. In this report, critical habitat is determined by population evaluations, or abundance, of *A. irradians* along a 50 m transect. Often studies that emphasis on environment association using regular tags, like shell chemistry, are lead in areas which sample sites are divided by ten kilometers or more to protect chemical and physical heterogeneity between sites [36-42]. Nevertheless, there is a growing requirement for methods that control the smallest

spatial scale at which important environments can be exactly distinguished using shell chemistry. Documentation of important environments is suitable for ecological reports that measure impacts of environmental modification on employment and survivorship, for controlling of serious environments, and for geographic provenance of seafood [43-49]. Now, we procedure elemental fingerprinting of shells to find optimal environment for *A. irradians*. In bivalve shells, mechanisms for combination of trace elements into carbonates containing components during shell growth change across species and life stage due to different factors and chemical and physical sorts of the environment [50-56]. Different physical and chemical factors in additional to the environmental factors can affect trace element speciation and bioavailability and so will affect the trace element configuration of the shell. Despite the effects environmental factors have on element incorporation, elemental concentrations have been used for several reasons including quantification of shell growth rates [57-60] as well as identification of natural environment, water chemistry change over time, enrolment success, stock structure, and movement patterns [61-65]. A recent study by a researcher [66] evaluated spatial flexibility in the elemental composition of larval mussel shells [67-71], and showed that spatial resolution of the source was possible at a scale of 10 km. Up to now no one applied elemental fingerprinting to determine the location of critical



habitats for bay scallops.

The aim of this study was to estimate if elemental chemistry of *A. irradians* shells, a fast growing species, can be used to recognize areas expressed by scallop population. Scallops are the only bivalves that have the capability to swim in the fully-grown phase making renovation of their life histories more complex than for other species. We advanced a methodology for classifying environmental links of vital *A. irradians* environment features at a significant three-dimensional resolution. The environmental parameters classified in developed environment that could control strategy of this commercially important sorts. Furthermore, this study focuses on a well understanding of issues that control the trace metal chemistry of *bay schalop* shells . Results of this studymay support to better recognize the relation between the environment and Me/Ca ratios.

### **State of the art**

Information of past environmental and climate changeability is one of the main facets to model probable changes in the future. The reasons why bivalve shells gotten so much popularity can be summarized as follows [72-78]:

(1) Shells offer completely aligned archives of their environment [79].

(2) Multiple methods such as shell growth rates, isotope ratios and minor elements can be used for the environmental data [80].

(3) Various shells of long-lived bivalve species like *A. islandica* can possibly offer century long environment histories.

(4) The wide distribution makes shells perfect ecological recorders.

In the early days and before instrumental progress, the geochemistry of bivalve shell can possibly offer measurable data on environmental [81-91]. Nevertheless, studies of shell geochemistry after more than half a century, the changes in trace elemental are still not well recognized and trace elemental proxies are not regularly applicable. To address this fact:

(1) The mechanism which controls the procedure of acidification of the ocean is mainly indefinite, but has a great impact on the amount of trace element in shells [92-94].

(2) The correlation between various trace elements is not well realized [95-98].

(3) The special effects of non-environmental issues controlling the elemental distribution in shells have not been calculated, and deduct all the other signals from the original environmental signal would be difficult.

The most key results of shell chemistry studies on bivalve shells and also qualifications and challenges are as following:

(1) Stable isotopes. Hiding the bivalve shells in oxygen isotopic equilibrium with the normal pH water is the main function [99-105]. Metabolic action utilizes no influence on the oxygen isotope fractionation during the shells mineralization [106-115]. Consequently, the oxygen values of bivalve shells can be used to rebuild various temperature. Several studies have effectively used this pattern to conclude past temperatures [115-121]. Nevertheless, the consequent oxygen temperature renovations need understanding of the oxygen value of the water that the bivalve could stand on it. This importance highlights the great alert and is seldom identified. Variances of shell oxygen isotopes may consequently show changes of normal pH water temperature as well as pH.

In compare to oxygen isotope, stable carbon isotopes are more difficult. They may be determined by many environmental factors. Due to the release of the lighter isotope, the amounts of carbon isotope in the shells compare to their regime are typically more positive [122-134]. The fraction of carbon reduces with age. Nevertheless, because the food and dissolved inorganic carbon are related with pH and also seasonal changes, the values of carbon isotope in bivalves can be a good representative for

the environmental and climatic factors [135-139].

(2) Trace elements content

(a) Physiological issues are commonly accepted as an factors that can affect the incorporation of **Strontium** into bivalve shells [140-146]. Additionally, in winter and imitation lines, Sr is intensely developed in the major growth lines [147-151]. Shell growth rate could control the Sr concentrations of bivalve shells [152-155]. Beside these affects, environmental and climatic signals, such as information on the normal pH water can be obtained by evaluation of Sr variation of bivalve shells [156, 157], and pH [158]. In addition, different elements calcium ratios could reperesent an environmental factor. For instance Sr/Ca ratios are a good representative factor for the ocean temperature [159].

(b) **Magnesium:** several factors including temperature [132, 145, 158], ambient water chemistry [18, 59, 112], crystal morphology [20-23, 45, 52, 73-79, 110, 134], species [115-124, 138], shell growth kinetics [140, 148, 152-159], physiological procedures [1, 15, 75-79, 90, 125], ontogenetic age [26] and diagenetic [160] can effects the magnesium ratio of bivalve shells.

(c) **Barium.** The amount of the Ba/Ca values of bivalve shells might be a representative factor for salinity or other environmental properties [125,

134-139, 150]. Furthermore, depending on the age, growth rate, ontogenetic and other unknown environmental factors, the amount of Ba can be different from one species to the other one [152-160].

(d) **Sodium.** Na concentration is the best factor to show temperature [120-125]. Lattice defects could be a place for Na ions accumulation and can also be absorbed onto crystal layers [155-158, 160]. By comparison the Na content in the shell in the polluted water and fresh water, it has been reported that in the first one the Na concentration in shells is lower [160-163].

(e) **Manganese.** Soft tissues of bivalves have the highest Mn content [163] in compare to the shell. Shell deposition rate strongly affect its concentration [164]. Four factors can define the Mn concentration:

1. Taxon [29]
2. Growth rate [31-33, 45, 83]
3. Environmental changes [26-91, 112]
4. Diagenetic method [256, 162]

The Mn concentration in bivalve shells is not an absolute representative factor for the metal concentrations in the source water. In the shells, high concentrations of Mn is also similar to Ba and they both can be related with biomass production [165-168].

(f) **Lead.** Previous authors reported a special trade for the accumulation of Pb in the bivalve shells. Many studies investigated the amount of the Pb in the shells and reported that the amount of the Pb in the shells were always greater than those of the soft tissues. There is an intense correlation between shells components and the Pb level and it could be applied to record the ambient Pb contamination [169]. The concentration of Pb in the organic matrix in bivalve shells is like that of the carbonate crystal [170]. Environmental parameters could define the Pb concentration in bivalve shells and Pb in bivalve shells can be applied to record the environmental factors as well [171].

(g) **Boron.** The best place for the accumulation of the boron is the inorganic section [172]. Many factor such as environmental factors can mainly regulate the B scattering in bivalve shells [173]. In particular, while shells grew, it was found a relation between pH and boron content [174]. Its relation to the temperature has not been proofed yet.

(h) **Copper.** The previous investigation showed that there is an equation trade for the Cu concentration in the bivalves. Different investigations in the past showed that Cu content in soft tissue is much higher than in shells [175]. The amount of Cu in the shells is the key factor to to track the Cu contamination in the atmosphere. shell growth, temperature and pH cannot affect the Cu concentration in bivalve shells [176]. Moreover,

Cu distribution can be strongly influenced by physiology in bivalve shells.

(i) **Zinc.** The Zn concentration in the shell is much higher than its amount in the soft tissue, but it is absolutely more than the Cu amount in the ambient water [177]. The amount of Zn in bivalve shells is directly related to the composition of the ambient water. Previous study illustrates that there is no correlation between Zn and shell growth but the other mechanism such as inner biological mechanisms control the amount of Zn. Concerning the impact of the other factor there is no common agreement between the researchers. For instance concerning the impact of the age and Zn there is two opposite reports, one showed the Zn level of bivalves decreases with age, while the other suggested that the concentration of Zn enhance a little with age.

(j) **Iron.** Another element that has higher concentration in soft tissues than in shells is Iron. The key controlling factors on the Fe spreading in bivalves are:

1. Ambient environment
2. taxonomy
3. ontogenetic age
4. physiological mechanisms
5. diagenesis

(k) **Chromium.** The amount of Cr in soft tissues in bivalve shells is higher than in sediments. Cr concentration is a good representative factor for the water composition that shells lived in. Physiology can have the same effect as environmental parameters on the concentration of Cr in bivalve shells

(l) **Silver.** Ag accumulation in the shells is much more than in the soft tissues. Again Ag concentration in the ambient water can show the Ag concentration of bivalve shells.

(m) **Aluminum.** Opposite to the other elements Al content are more accumulated in the in soft tissues of bivalves. Previous studies from different authors suggest an intense relationship between the amount of Al in shells and the environment Nevertheless, one study claim that the is no correlation between the metal concentration in mussels and the metal concentrations of the water that they lived.

(n) **Cadmium.** Similar to Al, Cd has higher content in soft tissues of bivalves than in shells. Nevertheless, previous studies applied the easy substitution of Ca by Cd to demonstrate that Cd is concentrated in shells. Apparently, in soft tissues, Cd concentration shows a link between Fe and Zn. In bivalve shells, the concentration of Cd in the organic matrix is quite similar to the one in the carbonate crystal. The factors that can illustrate the Cd distribution are:



1. Physiology
2. Environmental changes

Hence, Cd looks to be a suitable proxy of metal contamination of the water.

(o) **Cobalt.** Co has also apparently higher concentration in shells than in soft tissue. The Co concentration and shell size showed a differing power role. Moreover, the Co concentration is also determined by biological factors mentioned in the previous section.

(p) **Nickel.** In the case of Ni in bivalves, this element has a higher content in the shell layer than in the soft tissue. The Ni concentration of bivalve shells is a good representative factor for the seasonal changes. There is no strong connection between Ni in the shells and in sediments but amount of Ni in the bivalves can be effectively applied as a bio-monitor for metal pollution.

(q) **Vanadium.** Most of V absorbed in the surface of the shell and only small amount of V is observed in the bivalves. The amount of V in bivalve shells show spatial and temporal variations affectively.

(r) **Rubidium.** Rb concentrations in bivalves shell are good representations of the Rb composition of the water. There is not obvious periodicity of Rb levels was observed in bivalve shells.

(s) **Mercury.** The Hg content in bivalve shells is also affected by physiological factors. The amount of Hg in shells seems to be a suitable indicator of environmental Hg contamination.

(t) **Selenium.** Se concentration in the ambient water strongly affects the Se factor in the shells. Therefore concentrations of selenium in the bivalve shells could represent the composition of the water that they lived.

(u) **Sulfur.** S and Mg both could control the elongation of the crystal and are the main component of the bivalve shells. It should be mentioned that S content decreases with the age of the shell. High levels of metabolic activity can be caused by high contents of S. By measuring the S content, the effects of anthropogenic on the environment could be traced.

(v) **Fluorine.** The annual spawning period could be proved by high fluorine contents in mollusk shells. By considering the difference in the pattern of fluorine and strontium, it has been shown in the previous studies an overlap between the peaks of F with those of Sr in the spawning line

### **Studied shell and its location**

English explorer Bartholomew Gosnold first discovered the island of Nantucket in 1602. At that time the island was a dependency of New

York until it became a dependency of Massachusetts in 1692. The first immigrants came from Massachusetts and New Hampshire in 1659 and lived alongside about 3000 Wampanoag natives. In the 1690's Nantucket began to change from a society of tiny farms to a society affianced in whaling from tiny boats and by 1715, deep sea whaling had begun. The island finally became the whaling capitol of the world. In the period of 30 years starting in the 1830's, however, Nantucket's economy was "brought to its knees". Whaling trips had become increasingly luxurious, the whaling boats could not become past a sandbar that had formed at the opening of the harbor, and the American Civil War took numerous of the men far from fight for the Union army. Nantucket was finally protected by the salary of summer tourists and finally get one of the best well-liked tourist termini on the east coast. The bay scallop industry was also a factor in the renewal of Nantucket as scalloping get an essential part of the economy; it now brings in about 2 million dollars each winter during times of highest harvest.

### **Importance of the Nantucket Harbor**

Nantucket Harbor is super important to the economic and social well-being of the island – it is a source of shellfish and other seafood, it charms travelers on the ferries, and its beaches are a main fascination for various of the island's tourists. The harbors of Nantucket have been

supplies of shellfish, especially bay scallops, since the 1800's; previously, scallops were applied only as tempt for cod fishing. Later in the 19th century, scallops had gotten a general attractiveness and Nantucket citizens started to harvest the abundant bay scallops and sell them off-island. Unluckily, as an effect of variations in water quality, the habitat terms and prolificacy of the shellfish have altered by time. Several fishermen tell that "bay scallops so plentiful, which you had no method to avoid pacing on them when you entered the water". Currently, bay scallops are not practically as popular as they once were. In the 1980 season, commercial scallopers caused in 120,000 bushels of scallops, but in 2007 they caused in an all-time low of 3,860 bushels. 2008's harvest was back up to 17,000 bushels, and 2009's harvest was back down to 9,000, showing the variation of the harbor's scallop population. Despite the variations in the populace of shellfish, Nantucket's bay scallop fisheries stay an essential quantity in the island's economy. Not only do they offer shellfish for the citizens, tourists, and firms of the island, they are one of the few trustworthy sources of bay scallops for the United States. Nantucket's bay scallop fishery, although "less expectable and creative than it once was," is still a dependable supplier of bay scallops to the rest of the country.

Nantucket's budget has also trusted deeply on its tourists since the late 19th century. At summer, which is high season, there can be up to 60,000 people on the island, but the year-round populace of the island is around 15,000 (Town of Nantucket). This number varies due to the temporary nature of the populace; even some "permanent citizens" spend long time of the year off-island. Several local businesses on the island are open only during "high season," that is in fact the Memorial Day to Labor Day, therefore they trust on the island's summer tourists to visit their businesses and hold them in business. Moreover, up to 89% of the taxpayers on the island are non-resident property landlords and is on-island only during the high season.

### **Nantucket Harbor**

The Nantucket Harbor Estuarine System is placed inside the Town of Nantucket on the Island of Nantucket, Massachusetts. The relatively virgin nature of Nantucket's near shore and Harbor waters has historically been a worth benefit to the island. Nevertheless, attention over the possible mortification of Harbor water quality starts to begin, that caused in observing, technical studies and administration design that lasts to this day. Nantucket Harbor is one of the major covered bays in southeastern Massachusetts and one of the rare with a quite high water quality qualified of supporting important high quality ecological habitats, like

sustain a scallop fishery. Fatefully, it is the virgin nature of this method, that could ultimately threaten its ecological health as the coastal waters throughout Southeastern New England get gradually degraded, and the difficulty for approaching and development of remaining great quality environments enhances.

The system has been connected to a northern shore by water from Nantucket Sound (Figure 1). The division for this embayment system is spread completely in the Town of Nantucket. The potential long-term influences resulting from the gradually enhancing division based nutrient feedbacks, mainly from stimulants, on-site poisoned care and enhanced side runoff related with enhanced coastal progress has just been recognized as a main threat to the health of our coastal waters and that of Nantucket Harbor. Because of the possibly long time lags between nutrient linked activity within coastal divisions and the influences on coastal waters, important nutrient linked water quality degradation can be started before the effects become noticeable. In the case of Nantucket Harbor, important in keeping the water quality within this procedure is the glowing rate and tidal exchange with the high quality waters of Nantucket Sound.



Figure 1: Major component basins of the Nantucket Harbor Estuary assessed by the Massachusetts Estuaries Project relative to nutrient related habitat health and nitrogen management planning. The Harbor exchanges tidal waters with Nantucket Sound through a single jettied inlet. Freshwaters enter from the watershed primarily through direct groundwater discharge and a series of small, short streams draining wetlands and 1 small surface water discharge

The morphology, or physical shape of the harbor is due to three main processes: glaciation, marine erosion and marine deposition. In general Nantucket owes its life to the late Wisconsin glaciation. At Nantucket the

central ice sheet got its maximum southern level about 21,000 years ago. This occurrence is noticeable by the terminal Nantucket moraine, that stretches from Monomoy southeastward through Sankaty Head and could be recognized by the naturally hilly, hummocky terrain named the Shimmo Hills. Melt water streams delivering from the icy facade accumulate sandy outwash plains to the south and southwest of the moraine that, mixed with the somewhat fresher outwash deposits across western Nantucket, include more than two-thirds of Nantucket's surface.

In a quite small period of time after 21,000 yrs B.P., the glacier entered the period of stagnation and retreat. The erosion of sea level grow and the marine flood of the Nantucket Sound area have removed most of the evidence of this method, therefore the subsequent series of activities is slightly risky. The glacial face retreated, first to a line a few kilometers north of the terminal spot, and farther north to Cape Cod. To the north of the moraine in the different zones are a mixture of outwash, ice-contact and glacial lake-bed sediments placed down through the first of these stagnation-retreat actions (Figure 2). Outwash deposits through the western part of the island also were deposited at this time. Several isolated residue blocks of ice were hidden in sediments during inactivity/retreat and the following melting of these blocks created depressions called kettles. The location and bathymetry of Sesachacha



Pond propose it was perhaps formed this way. Lower areas of the Head of the Harbor and Quaise may also have been ice block kettles.

Main part basins of the Nantucket Harbor Estuary evaluated by the Massachusetts Estuaries Project relative to nutrient linked habitat health and nitrogen management planning. The Harbor exchanges tidal waters with Nantucket Sound across a particular jettied inlet. Freshwaters arrive from the watershed primarily over direct groundwater discharge and a sequence of minor, little streams draining wetlands and 1 tiny surface water discharge.

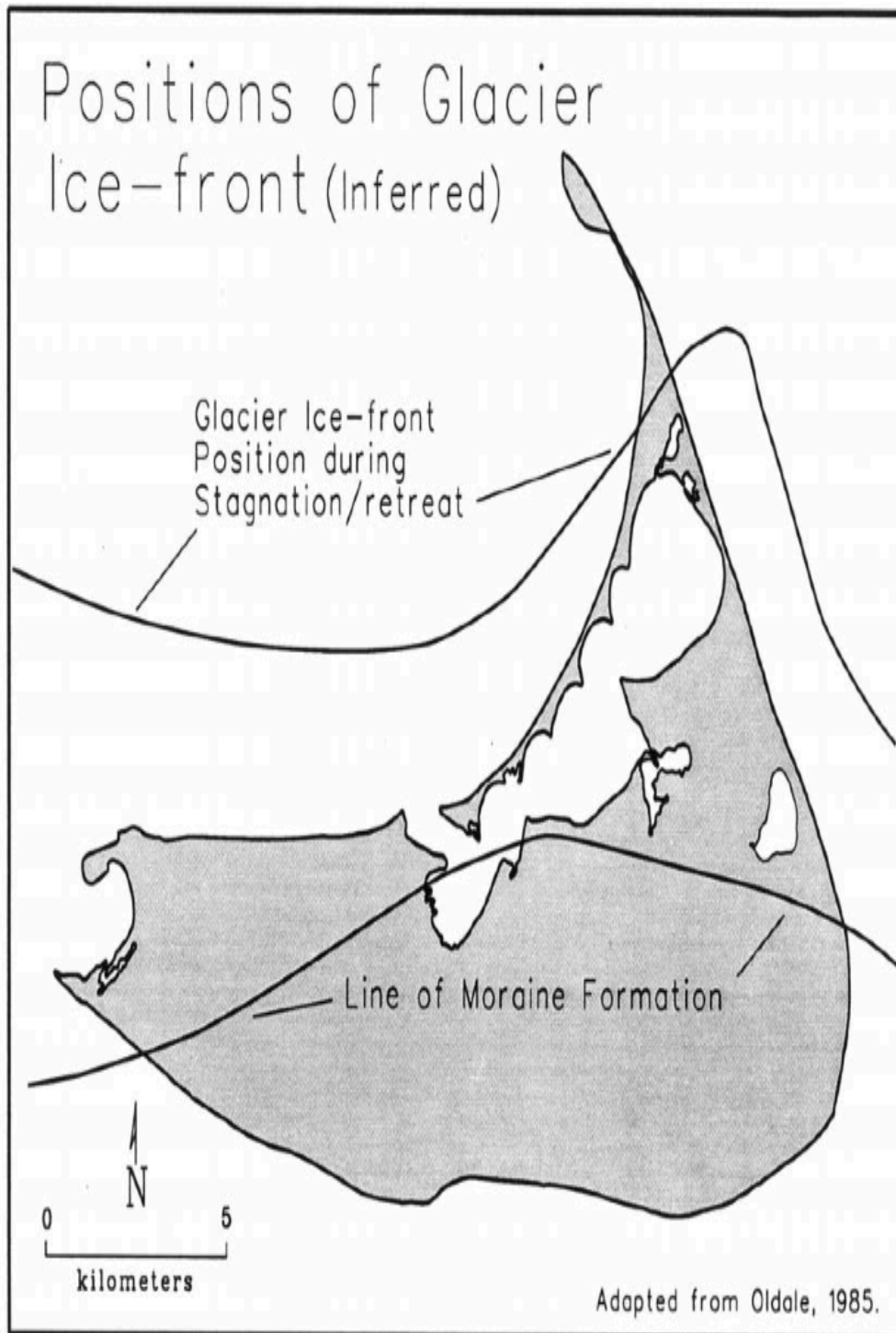


Figure 2. Basic map of ice sheet front relative to Nantucket (after Oldale 1985). The southern route shows a site for the establishment of the Nantucket Moraine. A more southerly highest terminal extension is not illustrated. The northern stand of the disappearing ice layer was essential to the creation of harbor area residues; moreover there is proof of glacial lake-bed deposits in Polpis Harbor and a pro-glacial lake in the harbor area.

The residues that form the structure of the island are unconsolidated and simply eroded by waves, leading to a constant variation in the island's form. The residues series from organized outwash sands to fine soils to gravel linked to moraine sediments. Overall, the southern coast of Nantucket has been worn while the northern coast has been the zone of marine deposition. Primarily, the Harbor was perhaps public for the northwest and limited to the northeast by a tombolo bonding Coskata with the Wauwinet zone. The structure of Coatue by beach deposit and spit extension changed that was possibly a shallow open bay into the current tidal lagoon with a thin controlled inlet.

Coatue is completely created of beach and dune sediments, that have been worn and moved from elsewhere. The best possible sources for this residue were sediments in the area of Coskata. The slight bluff encrustation in the Head of the Harbor at Coskata is a trace of more wide glacial ice-contact residues related to the first recessional site of the glacier. These and surrounding, now eroded sediments to seaward perhaps produced a sediment source for the regular extension of Coatue spit towards the current Harbor mouth (Figure 3).

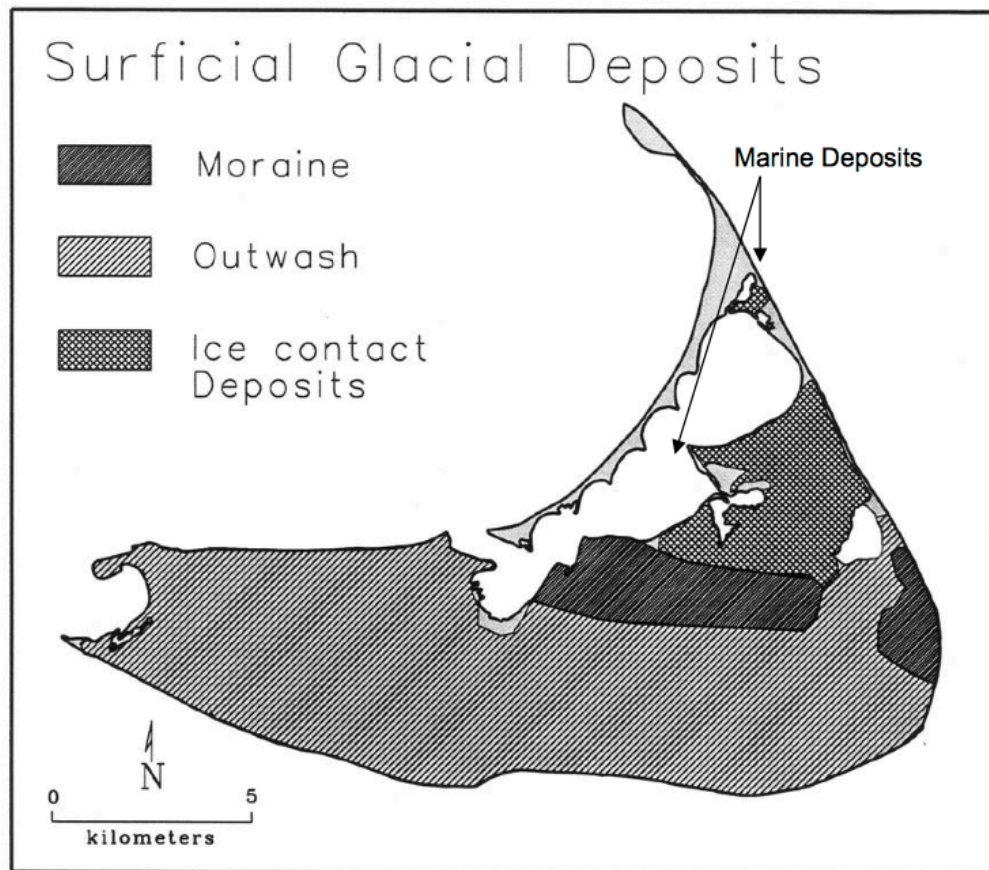


Figure 3. Universal division of surficial glacial residues on Nantucket (after Oldale 1985). Wide sediments of sandy outwash are the effect of some depositional occurrences stemming from diverse ice-front sites. Several of the freshwater and saltwater wetlands in the Polpis Harbor zone happen in regions of irregular ice contact (uplands) sediments and tiny grained, glacial lake-bed sediments of lower hydraulic conductivity. Coatie and Great Point are marine residues produced as sea level rose post-glaciation and coastal methods are constantly alteration that.

We chose Nantucket Harbor principally because of its imperative commercially fished bay scallop (*A. irradians*) population. Commercial populations of *A. irradians*, in Massachusetts (MA), happen in the waters of Cape Cod and the Islands. Landings of *A. irradians* in MA have dropped quickly throughout the last two decades from a average of 399 metric tons (\$1.4M) in the 1980's to a average of 47 metric tons (\$1.1M)

from 2003-2010 (NMFS data; no data 1997-2002). As landings have dropped, the market importance of the MA *A. irradians* has improved. The market cost and import force (especially from China) have directed to a major expansion in coastal aquaculture study focused on the *A. irradians*. Besides the important investments in aquaculture and seeding plans to enhance recruitment and age period yields, we recognize fairly slight about the movement patterns of *A. irradians* in Nantucket Harbor.

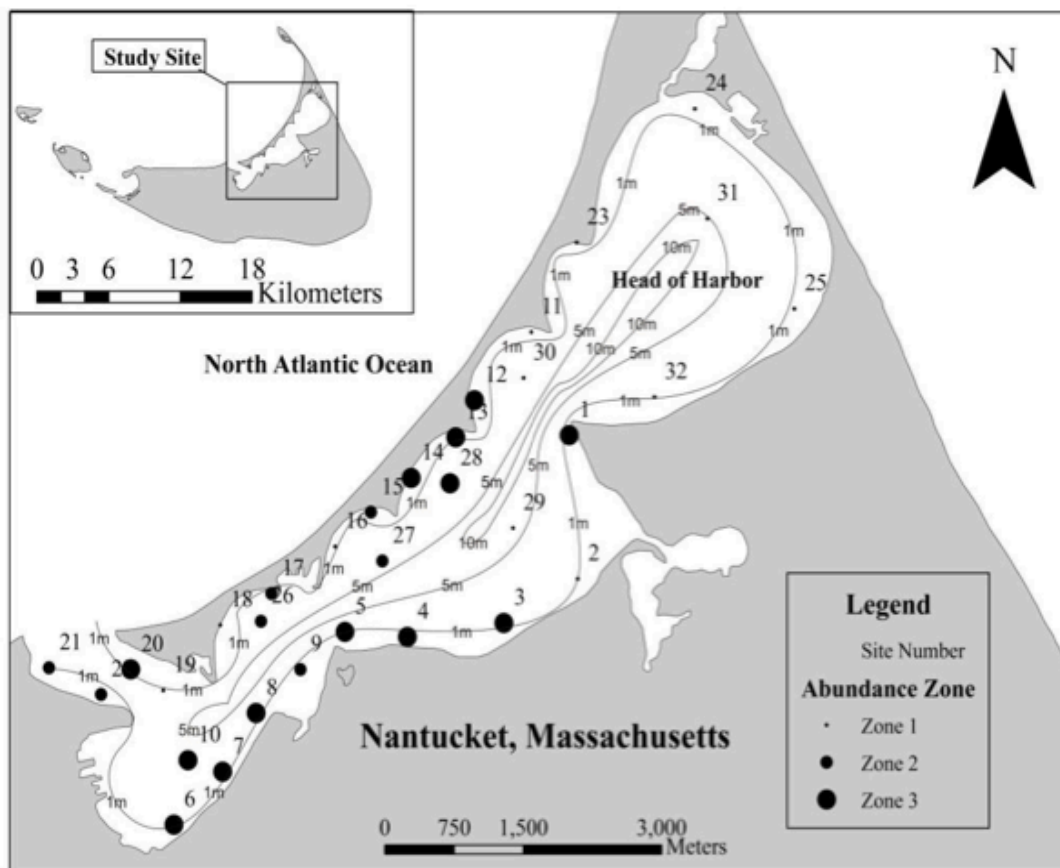


Figure 4: Collection sites in Nantucket Harbor (August 15th – September 15th, 2013). Abundance areas illustrated by circle diameter, which the maximum abundant spots are shown by the biggest circle, and spots that no scallops were discovered are shown by dots. (C.I. 2m)

Nantucket Harbor (Massachusetts, USA; Figure 3) is roughly 10 km<sup>2</sup>, much smaller than other sites that shell-based trace element archives have been applied to rebuild life records of bivalves. The Harbor is assumed to be well mixed because of tidal impacts on the shallow basin and secured by severe ecological principles monitoring waste organization. Classification of locales relied on elemental analysis of *A. irradians* shells from individuals collected at several places in Nantucket Harbor. By these records, we formed a binary logistic regression model that allowed identification of source habitats and exposed a series of salinity and pH conditions that help high abundances of scallops.

## **Experimental**

### **Sampling and sampling sites**

Sites and quantity of scallops retrieved obeyed the sampling rules of the Nantucket Shellfish Management Plan (<http://www.nantucketharborplan.com/>). In this research water sampling happened between 9 a.m. and 11 a.m. to decrease the number of issues affecting pH, that is identified to variation throughout a regular cycle. We investigated 32 locations (Figure 3) from mid-August to mid-September in 2013 for the subsistence/absence of bay scallops (*Argopecten irradians*). Twenty-two sites had adult scallops existing (Areas 2 & 3, Figure 2-1). Four of these spots also had juveniles (Areas 8, 13, 19, and

30) and ten were barren (Area 1, Figure 3). In situ measurements of base water quality were also prepared at the period of collection. All spots were well oxygenated ( $> 6.0$  mg/L dissolved O<sub>2</sub>) with a temperature range from 22.4°C to 26.5°C. Thirty adults were collected by the types from both of the Area 2 & 3 spots. When juveniles (spat; average shell height of 10.5 mm) were observable we collected a minor number. Different also documented overall scallop abundances on the 50-meter physically taped transect line at every spot. The analytical threshold for area documentation was described by separating regions of described abundances,  $n = 71$ , this amount divided three areas: Area 1 (no scallops), Area 2 (between 1 and 70 scallops), and Area 3 ( $> 70$  scallops) (Figure 3). The mean value of individuals was 71 and the average regularly differentiated amongst low and high abundant locations as determined by the shellfish directors at Nantucket. By this average rate we describe areas with scallops as low abundance (Area 2,  $< 71$ ) and high (Area 3, 71).

## **Analytical procedure**

### **Sample preparation**

For removing the soft materials in the shells, a Teflon covered spatula was applied. By using a non-metal brush, the shells were cleaned and

well prepared and stay in the 18.2 M- Ohm water for at least one hour. After this step by using ice-cold acetic, shells were washed for 60 seconds, and then the cleaning procedure followed by 2 step soaking the shells for 60 seconds in 18.2 M-Ohm water. Drying the shells is the next step, that's why the samples must be dehydrated during the night in laminar airflow at room temperature. Each shell should be cut by a blade from an umbo to growing edge, which is the most important part of the shell for LA analysis. Figure 4 shows the different part of shell.

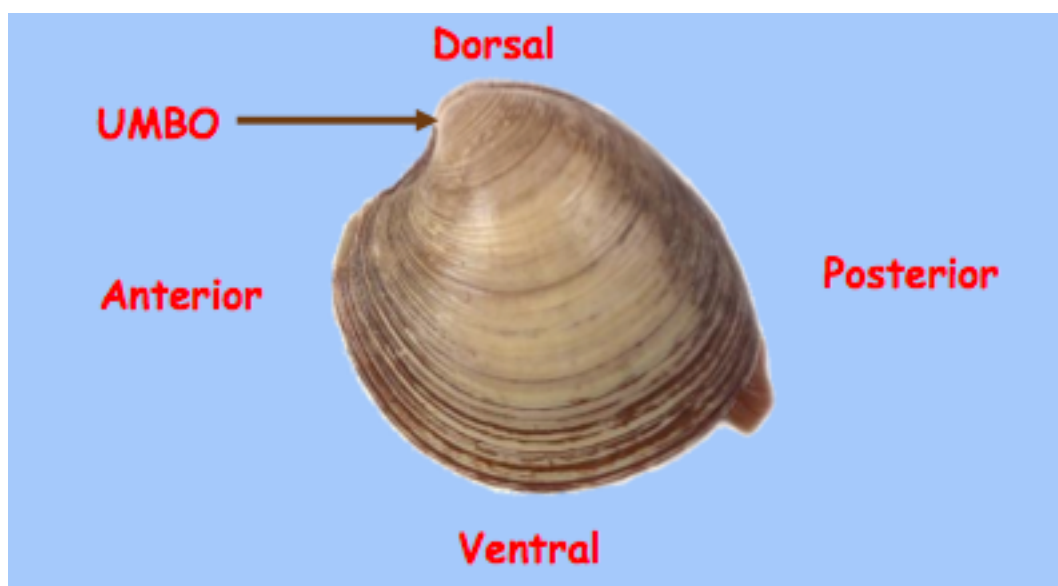


Figure 5: The full schematic view of the different shell section.

### **Elemental analysis by LA-ICP-MS**

For applications involving understanding of the spatial variation of elemental content in various samples, the LA-ICP-MS technique is



especially suitable for in-situ analyses of trace elements. A schematic of LA system is shown in Figure 5.

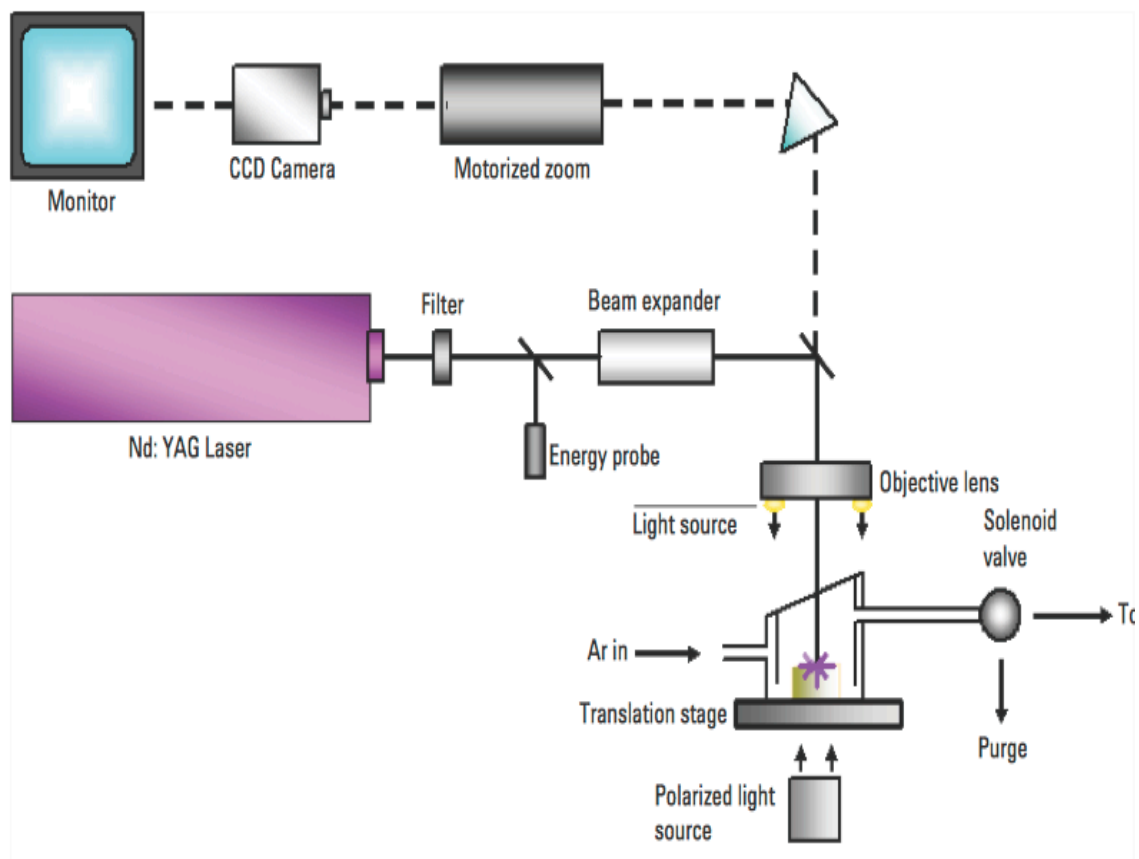


Figure 6: A schematic of LA system.

A piece of the shell from umbo to the growing edge was prepared in a thickness of roughly 2 mm and, by an IsoMet® diamond saw blade (Buehler Diamond Wafering Blade Series 15 LC blade) on an IsoMet® low rate saw as shown in Figure 6.



Figure 7: IsoMet® diamond saw blade for cutting the shells.

Firstly, samples were fixed on a Plexiglas cube and a quick-drying adhesive which were used to fix the shell on the Plexiglas and get it ready for cutting with the blade. For each shell ca. three-millimeter-thick pieces were cut with a low-speed saw (Figure 7). By fixing the cross-sectioned pieces on glass slides, and polishing by a Buehler G-cloth with 1  $\mu\text{m}$

Al<sub>2</sub>O<sub>3</sub> powder and finally ultrasonically washing in Millipore water, samples are ready for LA analysis. An overall of 5 thin pieces of fully-grown shells per location were ready. After ablation of this piece by LA, positive charged ion produced and measured by detector to investigate the amount of various trace elements in the shell (Figure 8).

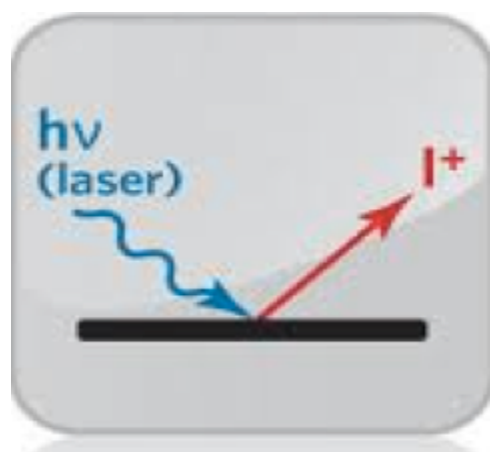


Figure 8: Shell umbo to the edge after cutting the shell, this section was investigated with LA-ICP-MS.

Figure 9: Ion production by LA.

The LA-ICP-MS instrument used in this work contained of a laser ablation method (213 nm Nd:YAG; Cetac Technologies, Omaha, Nebraska, USA) linked to a Perkin Elmer ELAN DRC II ICP-MS (Perkin Elmer, Norwalk, CT, USA) (Figure 9).



Figure 10: The LA-ICP-MS instrument used in UMass Boston laboratory.

Various isotopes were checked to investigate elemental content in the shell. Recording the analyte signal was done by a line scan near the edge by a spot size of 150  $\mu\text{m}$  at 20  $\mu\text{m}/\text{sec}$ . A GeoPro2010 Software (Cetac Technologies) was used for Signal managing. Two different calibration standard were used in this study, MACS-1 and MACS-3, which were, evaluated 3 times each at the start of an study, and again every 15 samples. For further quantification  $^{43}\text{Ca}$  and  $^{46}\text{Ca}$  were checked as internal standards. By using Costech 4010 Elemental Analyzer, total carbon and

nitrogen on a form powdered shell material were also measured.

### **Statistical Analysis**

Normalization of each element to Ca concentration is the most important part for the start of the work. It was interesting to investigate whether elemental ratios could be applied to differentiate different locations or areas in the Port or not. In this aim multivariate statistics were applied for 35 samples from different areas with different level of abundance. By applying the records from full-grown and young scallops, the power of the binary logistic regression was estimated to properly allocate individuals to “area” across life periods. For preserving as much of the region (low/high abundance) discriminatory data as possible, the Binary logistic regression was applied. It must be note that the factor analysis should moderate the variables to the lowest potential number of uncorrelated variables.

Of the 4 positions, between 0 and 4 A. irradians individuals were plotted beside every 50 m splits. The harbor categorized in three regions according to the comparative population of scallops:

1. Region 1 – barren
2. Region 2 – low abundance
3. Region 3 – high abundance

None of the elemental ratios were originate to be statistically diverse in fully-grown shell edges among locations. For fully-grown shell, the ratio of Fe, Cu and Mn are shown as good demonstrations of edge elemental ratios that are not statistically different. Comparison between different regions showed different Ca ratio levels for various elemental.

To investigate variances in water quality among scallop ANOVA was applied for various areas. By using ANOVA between depth and scallop abundance a statistical relationship was showed. According to our results, there is no real correlation between scallop abundance and bottom water quality.

Table 1: presents the accurate determinations of major and trace elements in shell samples by LA-ICP-MS

<b>Sample Name</b>	<b>Site</b>	<b>Shell Location</b>	<b>Ba/Ca</b>	<b>Co/Ca</b>	<b>Cu/Ca</b>	<b>Fe/Ca</b>	<b>La/Ca</b>	<b>Mg/Ca</b>	<b>Mn/Ca</b>	<b>Pb/Ca</b>
PO-1-GE	Pocomo	Growing Edge	9.35457	12.38189	12.19021	1377.76	0.514704	5629.694	333.648	16.04996
PO-1-U	Pocomo	Umbo	160.7265	131.7275	118.0978	5028.348	16.44579	24926.74	488.1852	40.37326
PO-2-GE	Pocomo	Growing Edge	18.66455	51.69132	27.36623	4308.983	0.837467	15175.11	4723.282	22.07416
PO-2-U	Pocomo	Umbo	8.036183	31.71904	66.89238	7837.549	2.510918	27557.44	3194.646	19.47085

PO-3-GE	Pocomo	Growing Edge	50.1785	345.4402	161.1795	16223.27	8.330989	63430.89	10439.38	300.3358
PO-3-U	Pocomo	Umbo	15.82785	43.85088	16.73757	7504.39	2.707982	35345.71	1265.274	14.7682
PO-4-GE	Pocomo	Growing Edge	2.123912	8.174766	11.91917	1534.868	0.120791	21091.01	807.4329	0.952767
PO-4-U	Pocomo	Umbo	3.26575	6.102633	10.8756	5659.985	0.291233	18420.31	293.9494	1.537315
PO-5-GE	Pocomo	Growing Edge	4.088155	13.3194	8.500834	2367.557	0.178179	8898.003	231.8986	4.655419
PO-5-U	Pocomo	Umbo	7.389481	1.528046	38.03584	258.2288	0.640752	1643.996	3702.866	0.942063
PO-6-GE	Pocomo	Growing Edge	7.166178	23.92009	10.58753	1021.555	0.375351	5338.527	1008.353	21.53752
PO-6-U	Pocomo	Umbo	5.452575	7.359726	20.62574	6053.099	0.790034	14867.01	488.6996	4.06813
PO-7-GE	Pocomo	Growing Edge	7.325727	28.04751	12.76255	1299.815	0.339448	5358.153	439.2818	13.97548
PO-7-U	Pocomo	Umbo	8.82839	44.41094	171.8584	9405.334	2.881058	27910.59	312.9173	7.555672
PO-8-GE	Pocomo	Growing Edge	1.776465	2.14104	20.44672	2405.171	0.152143	30022.93	2017.093	0.205008
PO-8-U	Pocomo	Umbo	3.799432	19.77174	21.16713	4518.489	2.013419	13609.3	304.6183	4.6961
PO-9-GE	Pocomo	Growing Edge	5.98618	2.716891	25.62815	1166.682	0.442331	21962.12	944.2859	8.503581
PO-9-U	Pocomo	Umbo	4.748529	5.368729	40.86496	2236.928	1.228591	5351.433	876.1664	2.335244

PO-10-GE	Pocomo	Growing Edge	4.242313	17.97684	5.608202	849.1876	0.134575	2663.392	216.5215	10.59651
PO-10-U	Pocomo	Umbo	5.000702	9.047769	21.57119	2094.605	1.099779	8953.412	833.0918	9.910623
PO-11-GE	Pocomo	Growing Edge	6.480769	16.8097	51.13524	1322.47	0.351283	12135.27	1258.119	6.216483
PO-11-U	Pocomo	Umbo	2.736479	2.917877	6.853187	3371.424	2.270881	29238.45	683.6025	0.546493
PO-12-GE	Pocomo	Growing Edge	5.73949	18.51964	12.8316	789.1285	0.129853	4217.272	277.1215	9.817527
PO-12-U	Pocomo	Umbo	3.848818	2.994407	19.28842	6649.898	0.401261	16131.19	288.0209	2.12698
PO-13-GE	Pocomo	Growing Edge	3.745895	2.62516	2.468884	1257.132	0.037408	15139	164.5523	3.315461
PO-13-U	Pocomo	Umbo	0.906153	0.369629	3.225303	1246.291	0.009012	19791	#DIV/0!	0.087111
PO-14-GE	Pocomo	Growing Edge	5.747278	12.55267	5.281682	807.7615	0.291625	21757.54	869.5142	3.101138
PO-14-U	Pocomo	Umbo	0.730729	2.976539	3.37023	997.5612	0.025642	18985.03	89.40884	0.213302
PO-15-GE	Pocomo	Growing Edge	2.80969	0.99423	35.91983	4838.538	0.050018	41481.43	1286.644	0.318665



PO-15- U	Pocomo	Umbo	2.265059	0.322325	5.480359	1930.01	#DIV/0!	38642.75	#DIV/0!	0.244033
PO-16- GE	Pocomo	Growing Edge	0.660646	9.85E-07	4.556905	1751.53	#DIV/0!	19728.78	#DIV/0!	0.058591
PO-16- U	Pocomo	Umbo	0.868039	0.334079	5.286588	886.0934	0.022588	16875.4	288.9011	0.089065
PO-17- GE	Pocomo	Growing Edge								
PO-17- U	Pocomo	Umbo	1.804227	1.145711	11.2207	621.7735	0.099568	54991.04	980.12	1.607023
PO-18- GE	Pocomo	Growing Edge	8.276938	42.87242	26.34884	1409.742	0.973237	6497.606	1569.039	19.6263
PO-18- U	Pocomo	Umbo	8.350712	4.328804	88.32423	327.3258	1.16079	4015.501	8583.106	0.830861
H-S-1- GE	Head Harbor S	Growing Edge	6.961833	50.4066	18.58389	1598.702	1.33299	11499.63	562.412	14.83322
H-S-1 - U	Head Harbor S	Umbo	30.42109	22.1558	84.68417	3296.387	1.095756	15556.8	1942.443	6.297715
H-S-2- GE	Head Harbor S	Growing Edge	6.780224	29.35705	15.85734	886.4385	0.773188	17513.86	293.9425	11.34849

H-S-2 - U	Head Harbor S	Umbo	7.637249	13.18684	17.88999	1040.296	0.442046	10946.4	1076.821	7.330652
H-S-3- GE	Head Harbor S	Growing Edge	4.41919	7.409598	212.9498	752.2978	0.333172	12777.73	276.5905	4.106934
H-S-3 - U	Head Harbor S	Umbo	896.4583	2291.695	1919.214	159266	65.4839	690474.3	96729.05	1866.207
H-S-4- GE	Head Harbor S	Growing Edge	4.618896	20.28842	10.10271	1027.881	0.23869	4949.407	206.7252	4.583756
H-S-4 - U	Head Harbor S	Umbo	8.255919	15.09255	30.86029	1647.662	1.241202	3503.571	2469.994	8.262746
H-S-5- GE	Head Harbor S	Growing Edge	5.05473	31.09852	12.09804	1340.324	0.70078	6191.84	316.8829	11.85791
H-S-5 - U	Head Harbor S	Umbo	5.885725	11.92083	55.97575	1546.239	1.129706	8378.039	1199.93	4.69646
H-S-6- GE	Head Harbor S	Growing Edge	4.482505	9.328111	16.98793	604.9803	0.429985	15897.63	625.7794	6.466557

H-S-6 - U	Head Harbor S	Umbo	17.63599	42.80206	206.9722	21952.88	1.357435	110340.5	4689.774	16.58576
H-S-7- GE	Head Harbor S	Growing Edge								
H-S-7 - U	Head Harbor S	Umbo	3.840368	5.565754	38.57589	527.3906	0.485357	5274.281	790.9947	1.871225
H-S-8- GE	Head Harbor S	Growing Edge	5.668925	18.4351	7.985753	1042.882	0.437624	4591.764	322.1681	19.56679
H-S-8 - U	Head Harbor S	Umbo	40.21972	87.89743	164.8141	7283.227	5.443537	25006.25	6291.867	41.14691
H-S-9- GE	Head Harbor S	Growing Edge	13.09215	25.08915	30.14335	2055.048	0.371401	12761.11	603.3862	11.92952
H-S-9- U	Head Harbor S	Umbo	#DIV/0!	31.22621	103.4198	776.3574	1.958281	292.2217	42192.52	4.215816
H-S- 10-GE	Head Harbor S	Growing Edge	8.75511	20.87488	41.23824	1520.039	0.580523	11012.1	938.0453	6.210688

H-S-10 -U	Head Harbor S	Umbo								
H-S-11-GE	Head Harbor S	Growing Edge	12.72512	56.19493	24.63158	3024.46	1.537623	4260.036	183.5628	29.73177
H-S-11 -U	Head Harbor S	Umbo	8.747288	26.58525	103.4836	5721.547	1.267547	6355.302	911.3918	11.83529
H-S-12-GE	Head Harbor S	Growing Edge	7.047791	30.94127	15.54828	1192.822	0.366745	7413.08	552.3619	13.4969
H-S-12 -U	Head Harbor S	Umbo	10.50965	10.56527	131.8574	1290.872	0.698142	4883.84	967.6719	3.867154
H-S-13-GE	Head Harbor S	Growing Edge	2.839032	19.83841	9.089443	886.9771	0.353765	5205.801	224.7809	5.301131
H-S-13 -U	Head Harbor S	Umbo	2.476969	14.03814	30.1115	2874.629	0.45019	8995.455	2616.786	2.447678
H-H-1 GE	Head Harbor H	Growing Edge	4.542369	16.38441	6.388531	738.2434	0.48148	5875.205	170.1237	5.592039

H-H-1 U	Head Harbor H	Umbo	5.223403	15.57246	21.82249	1824.22	0.869178	2267.198	486.2412	5.344764
H-H-2 GE	Head Harbor H	Growing Edge	5.458537	23.66352	10.96335	695.759	0.832446	3100.071	281.5864	14.25996
H-H-2 U	Head Harbor H	Umbo	4.426483	12.24185	4.175694	1036.877	0.809508	4308.878	170.1196	6.931045
H-H-3 GE	Head Harbor H	Growing Edge	7.486895	45.67958	16.13701	1498.263	1.392179	5163.296	412.2568	25.12863
H-H-3 U	Head Harbor H	Umbo	1.68324	4.853692	13.01868	4545.271	0.254474	15367.52	391.4075	1.719712
H-H-4 GE	Head Harbor H	Growing Edge	7.407731	27.42344	12.59351	1098.926	0.320816	6317.952	384.5342	14.989
H-H-4 U	Head Harbor H	Umbo	16.95668	42.85716	11.29488	4041.491	1.098175	26952.45	878.0211	17.05631
H-H-5 GE	Head Harbor H	Growing Edge	4.524929	11.10841	42.42769	1188.121	0.624754	12946.64	1368.464	2.864601

H-H-5 U	Head Harbor H	Umbo	7.916639	19.37139	15.50152	3602.808	1.380314	9119.728	155.4666	7.475497
H-H-6 GE	Head Harbor H	Growing Edge	5.922478	16.92324	30.52865	530.3497	0.784571	20317.14	747.8603	13.36095
H-H-6 U	Head Harbor H	Umbo	3.510884	4.134037	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	0.484505
H-H-7 GE	Head Harbor H	Growing Edge	4.642588	26.26226	23.29774	1181.528	1.168434	6303.738	181.8745	12.56878
H-H-7 U	Head Harbor H	Umbo	9.349213	18.85229	18.17623	986.555	0.535653	4571.212	1117.862	10.98746
H-H-8 GE	Head Harbor H	Growing Edge	2.428744	12.82732	31.24036	1160.503	0.692032	6929.16	634.0708	2.775167
H-H-8 U	Head Harbor H	Umbo	13.49874	84.13551	35.83088	8796.412	3.277056	19203.61	4522.932	15.65819
H-H-9 GE	Head Harbor H	Growing Edge	4.674624	17.10035	16.26291	943.8135	0.178783	12319.61	400.1561	12.37374

H-H-9 U	Head Harbor H	Umbo	1.564707	1.466407	112.879	1516.836	1.290318	3660.429	35835.34	0.548412
3rd-1- Ge	3rd Bend	Growing Edge	9.951172	24.8197	27.79737	1324.448	0.585694	22776.95	412.3775	22.87037
3rd-1- U	3rd Bend	Umbo	6.904863	18.9707	50.82547	3876.575	0.744676	18256.86	363.0578	7.242412
3rd-2- Ge	3rd Bend	Growing Edge	3.399832	2.359369	23.78789	1223.428	0.657235	68207.29	2246.504	0.700052
3rd-2- U	3rd Bend	Umbo	3.270594	15.97714	31.69677	6694.239	0.449662	29805.65	7215.15	4.851679
3rd-3- Ge	3rd Bend	Growing Edge	18.02229	13.03259	49.15318	1740.019	0.439825	50953.06	11794.93	2.46548
3rd-3- U	3rd Bend	Umbo	6.787516	17.1307	12.76275	1140.128	0.650047	23593.5	495.4454	6.850089
3rd-4- Ge	3rd Bend	Growing Edge	66.02122	101.9152	323.0353	1437.16	4.313835	54856.69	128727.3	17.74393
3rd-4- U	3rd Bend	Umbo	8.325686	17.57271	40.58369	6889.269	0.409636	26877.15	669.2744	5.057424
3rd-5- Ge	3rd Bend	Growing Edge	45.14339	93.0288	43.86076	1783.053	2.432962	16536.84	479.9313	48.63149
3rd-5- U	3rd Bend	Umbo	19.90573	56.8134	57.60857	269931.5	7.055517	23172.53	1261.182	24.823

3rd-6- Ge	3rd Bend	Growing Edge	16.65197	55.10421	14.95835	2090.909	0.75403	12822.32	364.6564	16.41596
3rd-6- U	3rd Bend	Umbo	12.66892	32.49906	13.53759	2811.307	1.323007	29893.65	214.6713	18.76574
3rd-7- Ge	3rd Bend	Growing Edge	5.502439	28.843	10.11427	945.9981	0.707248	6954.4	307.0936	10.61019
3rd-7- U	3rd Bend	Umbo	7.365148	40.45445	56.65737	9038.924	1.112252	7545.524	542.1262	11.71291
3rd-8- Ge	3rd Bend	Growing Edge	2.129467	1.216309	52.04034	515.1546	0.192783	22732.65	2037.022	0.341399
3rd-8- U	3rd Bend	Umbo	5.239696	6.898802	18.46926	1572.239	0.563513	20236.75	1117.287	11.14705
3rd-9- Ge	3rd Bend	Growing Edge	15.39124	24.91662	16.18297	1590.037	0.311313	18189.71	1214.531	24.41533
3rd-9- U	3rd Bend	Umbo	8.073303	25.00947	93.85662	7111.728	0.723244	19480.49	679.8195	11.64295
3rd-10- Ge	3rd Bend	Growing Edge	11.22994	40.01435	13.07585	1483.243	0.616577	9665.523	248.7334	16.98705
3rd-10- U	3rd Bend	Umbo	17.47568	14.73898	36.51475	1136.738	1.529443	11670.82	435.4475	7.576859
3rd-11- Ge	3rd Bend	Growing Edge	8.197779	27.04948	11.38869	884.6814	1.482873	6709.248	142.6767	16.51911



3rd-11- U	3rd Bend	Umbo	12.69122	41.69676	29.70571	4316.044	1.741854	21721.46	267.7681	19.40702
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Gathering of the elements in shell strongly depends on the area which shells have been formed. For instance the amounts of Mn, Pb and Fe in the shells showed the same amount as soft materials. Environmental factors such as pH, salinity directly affect on the accumulation of these elements in the shells. The various areas in the shells can define the differences in pH and salinity and subsequently the trace elements participate into the shell. Construction of a strong pattern that illustrates the relation between the ratio of different elements to Ca and physical properties of the water, which shells were living, is an important output of this study. In our investigation, the number of the A. irradians is expected to be meditative of ideal situations for both young and fully-grown A. irradians. As our documents were prepared in a short time they do not collect huge differences in water quality. Moreover, different elemental precipitation in the shells strongly depends on the depth of the area which shells are formed. Depth is different in the different parts of the port and especially at the front part of the port depth are much deeper and concentration on Mg and Ca is much higher. Furthermore, at the top of the Port, the protection is necessary for young shells.

In our investigation we see a direct relation between the elemental distribution in the shells and water pH. For by increasing the acidity of the water, Fe concentration is enhanced and therefore Fe/Ca ratios have the possibility to increase. Thus, ocean acidity can directly affect the Fe participation in bay scallop shells.

Therefore, shell chemistry for the young and fully-grown shells are necessary for different areas. According to the earlier study on the other carbonate materials, the variation in the pH intensely affected Ca ratio. The contribution of Fe in different shell layers is directly to the changeability in Ca ratio of shell. Shell chemistry is directly affected by water chemistry in different areas. Since formation of *A. irradians* at different ages need a sufficient time therefore its composition and its chemistry could be apply to investigate a pattern for the different areas in the port. Our investigation showed a valuable results that elemental analysis is valuable in classifying crucial locales in Nantucket Port.

By using the software, differentiate between Areas 1 and 2 can be observed and a controlling device to evaluate area quality for saving energies can be delivered. According to our data, for the area 3, 4 and 5 the quality of water should be maintenance. Therefore, the data provided by binary tool could let superiors to decide for scattering areas and also classifying areas for protection.

## Summary

1. Particularly in shell tip section, trace elemental concentrations of bivalve shells are influenced elemental ions in mother water which shells are formed in.
2. The selection of analytical techniques for trace elemental analysis, is very important particularly for the elements that are extremely enriched in organic substances, such as Mg.
3. Concentration of trace elements in the shells are directly controlled by shell organic substances. Shells which have high concentration of Be, B, Cu, Co, Pb are considerably enriched in Mg, as well as enriched in carbonate components. Normally element concentration in the initial shell layer is higher than the secondary layer. The cause of this elemental differences might be Due to the minor alteration in shell organic background in various shell layers, the concentrations of B, V, Cr, Mn, Co, Ga, Pb and U are somewhat upper in the initial layer than in the secondary layer, that those of Li, Mg, Zn, Sr, Sn and Ba illustrate the opposite. The causes why trace elements are spread inversely on the shells might be:
  - a. The variance in shell organic atmospheres qualities and content during existence

- b. The variance of physical and chemical sorts of trace elements
- c. Inter-reaction among them behaves contrarily in different shell numbers
- d. Trace elements monitoring for the shells in our investigation showed that:
  - i. Mn, Fe, Co, Zn, Ga, Sn, Pb and U have highly content in shells, while the remaining elements such as Li, B, Na, Mg, Si, P, V, Rb, and Sr are minimal.
  - ii. The amounts of Pb, Mg, Ca, and Ba showed a direct relation with the age of the shell while Cu and Si have a vice versa relation
  - iii. Size of the shells also has an influence on the elemental composition.

e. The main factors in describing the crucial living area of the bay scallop are:

1. pH
2. Dissolved oxygen
3. Temperature
4. Salinity
5. Depth

f. Due to primary reasons, the ventral margin of the shells should be prevented to be examined. Sr is more constant than Mg in the external level and central parts of the shells, and consequently could be a good substitution for climatic variation.

g. Due to high enhancement of Mg in the insoluble organic medium, wet chemical investigation are higher to in situ methods (such as LA-ICP-MS) for the analysis of the Mg concentration and new elements with an correspondence to organics.

h. Undoubtedly due to the various similarities to organics and shell carbonate, trace elements illustrate various sensitivity to environment, and consequently the substitutions of trace element-calcium ratios should be chosen suitably. Sr/Ca ratios are spicily associated to the sun spot number, surface air temperature. Mg/Ca ratios are just powerfully related to surface air temperature and solar irradiance. B/Ca is just connected with surface air temperature. Except for the surface air temperature, Na/Ca indicated different relation with sediment, the sea level stress. Mn/Ca is linked with the number of storms and sun spot quantity.

i. While trace elemental spreading of A. shells are established to be influenced various non-environmental and ecosystem controls, the connection roles among trace elemental concentrations (B, Na, Mg, Mn, Sr, and Ba) and shell ontogenetic year and growth rates might be affected

in the standardization to deduct the noise and to develop the ecological and ecosystem signals.

Characterization of important areas for the organization of significant shells resources like the bay scallop is important. Nowadays, all research centers in US are focused on increasing request for seafood resources by applying shell chemistry to start food origin and organization of marketable residents. For filling ecosystem and keeping the fishing nation, shell chemistry, characterization of ecological risk issues is important. Especially for Nantucket, MA it is important. Annual bay scallop arrivals to the beach in MA are expected at a rate of \$1.1M and are held within 4.8 km of the coast. By showing the financial significance of the bay scallop in MA and to Nantucket understanding the possible influences of environment variation on the residents is crucial.

The study existing here studied recent populations of the bay scallop in Nantucket Harbor showed that recreational and commercial harvest of the bivalve can be easily influenced by economy and culture. A sampling happened in 2009 to evaluate if geochemical marks in the shells can classify zones of the harbor that can host more shells. Once salinity was recognized as a crucial factor for the bay scallop and chemistry experiments with bay scallops in the water with high pCO<sub>2</sub> were applied to control how the shell can reply in upcoming situations of ocean

acidification projects. Consequently, bay scallop area is seaside estuarine and therefore endangered to variants in salinity due to freshwater release, it is essential to mention that in a low salinity conditions they are exist. This study investigates the response of the shells to severe amounts of acidified waters.

## **Outline**

There are two significant efforts that requisite to be focused in the near future. One is innovative statistics must to be manipulated to deduct the noise and renovate the ecological and ecosystem differences of the former time. The other is analyses that must be showed on the analysis of the procedure of biomineralization in bivalve shells.

Bay scallops, as they are geographically limited and their shell is combined of low-Mg, might help as an exceptional trade due to the variations in ocean pH. There are breaks in our knowledge of the calcification procedure, like the components presented in the organic matrix, and total ecosystem reactions to forthcoming ocean situations. Issues like temperature, salinity, dissolved oxygen, and pH all describe the value of habitats for a bay scallop, and eventually the sustainability of the population. These issues by themselves and in mixture influence the survivorship, net calcification rate, growth, reproduction, enrollment, and

finally the economic capability of the fishery. Nevertheless, various factors or mixtures of factors might be applied to estimate the value of a certain habitat.

Ocean acidification influences the net calcification of the bay scallop. Additional significant issues in evaluating the influence of future environment modification are temperature and salinity. As realized from documentation of fundamental habitats in Nantucket Harbor, there seems to be an ideal salinity for the organism that big populations of scallops lived. Upcoming analyses must be concentrated on controlling the joined results of these variables (pH and salinity) and model influences based on upcoming variations in both. It is important to determine to what level of calcification methods are linked through calcifying organisms. For instance, are the biochemical indicators just achievable in the bay scallop or could they prolong to other bivalves (e.g. mussel) or even into other calcifiers? Furthermore, for understanding and elucidating mechanisms included in the calcification method, multiple indicators would be established which supplement standing pressure biomarker study, like groups of amino acids, heat shock protein, glucose, and genetic changes.

Salinity and pH The reaction of survivorship and net calcification demand to be studied in reaction to a mixed water freshening and acidification of the ocean. A mixture of pH and salinity stages would be



studied. The overall method for the conduct would include setting up flow-through handling containers which paralleled the 4 pH handling level (7.8, 7.6, 7.4, and 7.2) with various salinity quantities (e.g. 30 and 15) in a nested extension plan which is consider as tank effects. Each pH level and salinity would be measured in triplicate. Measurements of pH and overall alkalinity would be prepared everyday for modeling, which the other carbonate structure constituents could be showed. To adjust for salinity, conductivity and overall deferred solid capacities would also be gathered. Seawater would be collected through small periods of time (< 6 days) when equilibrated to the pH and salinity situations and bubbled always to prevent. An accurate attention must be given to calculating the algal reply to these situations as intense pH and salinity settings may origin-opposing influence on feeding. Organisms would be prepared and keep for 7 days for acclimation to laboratory situations before starting of tests. According to the outcomes existing in this study, new treating would last 10 days therefore they can be related to the outcomes shown here.

In new calcifying types and comparison of plasma across calcifying types has not been studied. According to reported work on ocean acidification, organisms show various net calcification reactions are well-known and should be chosen for these kinds of study (for example negative response,

positive response, neutral, and threshold response). For instance, the bay scallop, shrimp, hard clam, and blue mussel all have different net calcification replies when tended at low pH. By a single aspect model as effected in this study for pH, the organisms might all be showed for the 10 days phase. During this period, organisms could be lost at time zero, day 6, and day 9 to measure plasma separated from blood testers. Plasma must be investigated for the ratios by different analytical instruments with a fluorescence detector. The subsequent numbers must be matched to net calcification percentages and pH handlings to control and also variations like seen now happened across calcifiers.

For example, growing organisms far from their natural habitat may synthetically enhance strains due to space limitations and low repetition of their natural habitat. While there could be natural differences in the accessibility of food in the wild, it is crucial to isolate the stress result initiated by week diet. Additionally, free amino acids are regularly applied to evaluate osmoregulation and bioenergetics, like amino acid profiles could classify species-specific physiologic replies to low pH.

This report helps to improve our understanding of the types of the bay scallop habitat and the subsequent influences of ocean acidification on calcification. Understanding the bond among ecological features and the results of environment alteration on calcification must be applied to

change geochemical signatures in prolonged food security guarantee methods. In this report both field and practical laboratory methods were applied to control the vulnerability of the bay scallop to ocean acidification in young and fully-grown life phases. It is important to mention that while estimates of future pH drop because of ocean acidification have been established, the final settings will just be recognized with time. However this report does not expect the upcoming existence or market influences for the Nantucket bay scallop under upcoming environment variation situations, it does notify our knowledge of the vulnerability of the bay scallop to these variations and offers setting for mitigation of effects over fortification of vital environment.

### **Shell preparation before LA-ICP-MS**

Shells gathered from the Nantucket were allocated ID numbers by specifying location and a number to specify number of shells gathered. For instance, a shell from location 10 that 15 individuals were gathered might be categorized 10 – 01 or 10 – 15, or any number between 1 and 15. Excel was applied to erratically choice that specific shells would be made for LA-ICP-MS. The arbitrarily chosen specific and location link were verified in a pad. The right tap was applied for all investigation. The significant difference is that for this kind of study the similar location should be applied between individuals to justification for physiological

changes in depositional amounts among the left and right tap. The explanation for preparing the sample will let for study of edge and umbo chemistry separately, but similarly for study by the life of the shell (umbo to edge).

For fully-grown shells, the rock saw in N-2-15 was applied. A cut to the minor left or right of the nub was prepared from the umbo to edge. For such samples, you are hand managerial the shell through the edge so it is essential just for big samples and 2 persons should be ready for security. A second slice must be done to one of the edges so that the shell is small enough to be appropriated on the micro cuts. Shells must be positioned in a sack and transferred to the IsoMet short rate saw now in M-1-23.

To follow the shell to the micro cut, Crystalbond was applied to join the half of the shell. A sharpy was applied to write the sample name onto the cut showing a "U" for umbo or "E" for edge. The particular umbo or edge was fixed next to the ID sign. Two cuts were applied from the fully-grown shells. The cut was set onto the IsoMet soft rate cut so that the knife-edge will make a tinny slice. It is essential to apply water in the pot to hold the knife-edge misty, and masses could be added to act a faster scratch. All slices were began on a speed of 3 till the knife-edge had effectively inserted the forward-facing and backward-facing of the slice, after first cut is prepared the rate could be changed up to 4. Small slices

were kept in a petrographic rack.

For young shells, Crystalbond could involve the full tap to the petrographic shot. Mount two diamond knife-edges on the isomet cut by applying a divider between the knife-edges. Adjust the shell so that the tiny slice to be found is between these two knife-edges. Since the young shells are usually not as dense as the grown-ups and two knife-edges are applied, it is essential to just apply small rates. Begin the knife-edge and gently drop the sample onto the knife-edge (Rate 2). Masses would be prevented for these samples. To do a fully the cut, you can increase the rate on the Isomet saw to 2. When the crystal is starting to engrave, the slice is ready. Rewarm the sample on a warm plate to remove the small slice and mount to an engraved petrographic cut showing what cut is umbo and what is edge.

Fully-grown and young shells need both be polished to a width which beam could go through for SEM. A soft side also supports for laser ablation output. For polishing, be sure that you have several types of sandpaper. Begin the polish with the coarsest one by addition of water to the top and do figure 6 shapes. The hand shape must eternally be a figure 6, but it is essential to converse the way to stop grooves in the shape. Finish it at the softest paper to excellently fine the top. Examine the shell below a microscope to realize if enough polishing has happened.

Now, the samples are prepared for LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry). This typical running technique won't contain modification of the ICP-MS or the hardware for joining to a laser. Nevertheless, an instruction for somebody who is doing the precise investigation offered in previous section is given. It is expected that a qualified laboratory specialist has previously started the laser head and began the software for the operator by doing the daily work on the ICP-MS.

On the software select the sample label and run the identification of your sample in Sample ID. Select the right technique for investigation by double clicking on the technique cell. This technique involves an automatic prompt for indicating the ICP-MS to begin collection. All test lists would begin with triplicates of every standard to be applied, for example MACS-1, and MACS-3 are quite suitable. Put the sample into the laser unit. For performing this, open the laser door and slowly pull out the sample unit. Screw the black lid to the right and take the previous sample out. Put sample fixed on a certain position so that the sample number is always at the top or bottom. Screw the cover clockwise to close it and slowly drive sample unit back into the shelter and tight the laser entrance. The helium gas must be enter to the system for about 30 seconds. Then decrease the helium flow to 250 mL/min and select load.

Increase the helium flow control on to 600 mL/min and select load. If you cannot enter the helium in this amount ask the laboratory specialist to set the system up for you. By applying the helium stream, you would be capable to prevent puffing the plasma on the ICP-MS out. Using software, join points to draw an ablation line. The technique shown here suggests ablating the prismatic layer. In this aim, the line must be begun on the shell nearby the nacre edge and must ablate to the periostracum. If you cannot find the spot for ablation, on the software try to find to Tools > Sample Mapping and select a 3 dimensional map. You should do the left click on the picture which your sample is going to be monitored. When you have the solid line, the software will give calculate the necessary timing for measurement. On the software, the measuring time must be longer than scanning time. On software, select File, and then save. Then select back to the sample part, highlight the sample to be measured, and knock Investigate sample.

2. Click go on the software, and then you can observe numbers achievement on the software, by selecting clicking the Actual Time tab.

3. Repeat the mentioned process for all the samples. Do series of more standards regularly (1 Seri per 10 samples). Record Calcium 43 and confirm whenever you investigate MACS-1. 15% signal

suppression means that analysis should be stopped and the ICP-MS and laser must be restart.

DigiLaz Method:

On the software, select the blue tab to start a method and select Single Line Scan.

Table 2. Conditions defined in software.

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LA-ICP-MS operating conditions	
Power	65%
Pulse Repetition Rate	20 Hz
Spot Size	25 $\mu\text{m}$
Scan rate	7.11 $\mu\text{m}/\text{sec}$

All data from this was investigated by applying software. The process presented here are basic rules to replicate with some direction from an expert operator.

Combination of data

4. Open the Excel file, assist this content on choices.



5. Select appropriate file. A worksheet will come up with the file name you selected.
6. Choose copy tab on the upper left of graph.
7. Change the lines on the software to classify zones to be combined.  
Mark the gas blank. Mark sample signal plateau. Mark the matrix.
8. Return to the worksheet with sample name, save it, and Click Done.
9. Return to the software. Repeat this procedure for the entire samples.
10. Select done tab on software.

### Quantitative Analysis

8. Select the Excel file.
9. Enter samples by selecting the first MACS1 and MACS 3.
10. By selecting the standard options on your page, label all the standards in the run. Load internal standard concentration afterwards.
11. Choose the zoom menu.
12. Select calibrations and set accuracy by the raw data.
13. Click measuring.

14. Normalized the data
15. Converted the data to molar ratios.
16. Calculate the relative error

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## WORK EXPERIENCE

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### Marshall Scholar

08/2013-01/2014

*School for the Environment, University of Massachusetts Boston, Boston, USA*

### University Assistant

10/2010-present

*Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Graz, Austria*

### Junior Researcher

08/2009-9/2010

*Bioenergy2020+, Graz, Austria*

### Project Manager

08/2006-07/2008

*Iran Polymer and Petrochemical Institute, Tehran, Iran*

### Laboratory Manager

10/2005-07/2006

*Fasa Azad University, Fasa, Iran*

## EDUCATION

---

### Ph.D. Analytical Chemistry

10/2010-present

*Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Graz, Austria*

### M.Sc. Analytical Chemistry

10/2003-09/2005

*Chemistry Department, Lorestan University, Khoramabad, Iran*

### B.Sc. Chemistry

09/1999-09/2003

*Chemistry Department, Bu-Ali Sina University, Hamadan, Iran*

## TEACHING EXPERINCE

---

*University Assistant, Graz University of Technology, Graz, Austria*

10/2010-present

Laboratory courses and graded exams in each semester

- Instrumental Analysis Laboratory
- General Chemistry Laboratory

*Instructor, Fasa Azad University, Fasa, Iran*



10/2005-07/2006

- General Chemistry I & II
- Analytical Chemistry I & II

## TECHNICAL SKILLS

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- Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)
- Graphite Furnace Atomic Absorption Spectrometry (GF-AAS)
- Flame Atomic Absorption Spectrometry (F-AAS)
- Thermogravimetric Analysis (TGA)

## AWARDS

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- First Place Poster Award, 2014 Winter Plasma Conference, Amelia Island, Florida, **USA**, 2014
- Student Travel Stipend, 2014 Winter Plasma Conference, Amelia Island, Florida, **USA**, 2014
- Marshall Plan Scholarship, Graz University of Technology, Graz, **Austria**, 2013
- 8<sup>th</sup> March Mobility Grant for Outstanding Researcher, Graz University of Technology, Graz, **Austria**, 2013
- First Place Poster Award, 12<sup>th</sup> Rio Symposium on Atomic Spectrometry, Foz do Iguacu, **Brazil**, 2012
- 8<sup>th</sup> March Mobility Grant for Outstanding Researcher, Graz University of Technology, Graz, **Austria**, 2012
- Outstanding Research by a Graduate Student Award, Lorestan University, Khoramabad, **Iran**, 2005

## LANGUAGE SKILLS

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- Persian (Native)
- English (Fluent)
- German (Intermediate)

## INTERESTS

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- Sport (Badminton, Tennis, Football, Basketball)
- Travelling (Getting familiar with new peoples and different cultures)
- New Languages
- Reading Books

## JOURNAL PUBLICATIONS

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- 5 Combustion of Volatile Organic Samples and Consequent CO<sub>2</sub> Removal Prior to Introduction to the ICPs  
**F. Moradi**, H. Wiltse, G. Knapp\*  
*Journal of Analytical Atomic Spectrometry, Under Preparation, Invited by the Journal*
- 4 Evaluation of the Oscillator Frequency of a Free Running RF Generator as a Diagnostic Tool for Inductively Coupled Plasma-Optical Emission Spectrometry  
H. Wiltse\*, **F. Moradi**, G. Knapp  
*Spectrochimica Acta Part B: Atomic Spectroscopy, 2012, 71, 48*
- 3 Electrochemical Synthesis of 6-Amino-5-(3,4-dihydroxyphenyl) Pyrimidine  
S. S. H. Davarani\*, N. S. Fumani, H. Arvin-Nezhad, **F. Moradi**  
*Tetrahedron Letters 2008, 49, 710*
- 2 Selective Homogeneous Liquid-Liquid Extraction and Preconcentration of Thallium Using

a new Calix[4]Pyrrole

A. R. Ghiasvand\*, **F. Moradi**, H. Sharghi, A. R. Hasaninejad

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- 1 Determination of Silver(I) by Electrothermal-AAS in a Microdroplet Formed from a Homogeneous Liquid-Liquid Extraction System Using Tetraspirocyclohexylcalix[4]pyrroles

A. R. Ghiasvand\*, **F. Moradi**, H. Sharghi, A. R. Hasaninejad

*Analytical Sciences*, 2005, 21, 378

## PRESENTATIONS

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- 8 Combustion of Volatile Organic Samples and Consequent CO<sub>2</sub> Removal Prior to Introduction to ICP-OES  
*2014 Winter Conference on Plasma Spectrochemistry, Amelia Island, FL, USA, January 6-11, 2014*
- 7 CO<sub>2</sub> Removal Using a Falling-Film Column in the Analysis of Organic Samples with Inductively Coupled Plasmas  
*SCIX 2013, Milwaukee, WI, USA, September 29- October 4, 2013*
- 6 Carbon Capture in the Analysis of Organic Samples with Inductively Coupled Plasma  
*12<sup>th</sup> Rio Symposium on Atomic Spectrometry, Foz do Iguaçu, Brazil, September 17 -21, 2012*
- 5 Effect of Carbon Dioxide-Loading on the Fundamental Properties of the Inductively Coupled Plasma  
*Colloquium Spectroscopicum Internationale XXXVII, Buzios - Rio de Janeiro - Brazil - August 28 - September 2, 2011*
- 4 Thermogravimetric Analysis and Devolatilisation Kinetics of New Biomass Fuels  
*18<sup>th</sup> European Biomass Conference and Exhibition, Lyon, France, 3-7 May 2010*
- 3 A Simple Homogeneous Liquid-Liquid Extractive-Spectrophotometric Method for the Determination of Fluoxetine in Urine  
*15<sup>th</sup> Iranian Seminar of Analytical Chemistry, Shiraz University, Shiraz, Iran, March 27-31, 2007*
- 2 Selective Homogeneous Liquid-Liquid Extraction and Preconcentration of Thallium Using a new Calix[4]Pyrrole  
*14<sup>th</sup> Iranian Seminar of Analytical Chemistry, University of Birjand, Birjand, Iran, August 29-31, 2005*
- 1 Determination of Silver(I) by Electrothermal-AAS in a Microdroplet Formed from a Homogeneous Liquid-Liquid Extraction System Using Tetraspirocyclohexylcalix[4]pyrroles  
*13<sup>th</sup> Iranian Seminar of Analytical Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran, 18-20 May, 2004*

REFERENCES ARE AVAILABLE UPON REQUEST

