A study of Mg/Ca in benthic foraminifera sampled across a large salinity gradient

Johan Gabrielsson **Dissertations in Geology at Lund University, Master's thesis, no 422 (45 hp/ECTS credits)**

Department of Geology Lund University 2014

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Cover Picture: Foraminifera counting. Photo Johan Gabrielsson

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Abstract: Multiple studies have found a link between Mg/Ca in foraminifera and various environmental factors (e.g Billups and Schrag, 2002; Dissard et al., 2010; Ferguson et al., 2008). This has allowed for paleoenvironmental reconstructions based on Mg/Ca in foraminifera to be made. My thesis has intended to find the influence of temperature and salinity on Mg/Ca in three species and one benthic Genus of foraminifera (*Bulimina.marginata*, *Globobulimina.turgida*, *Nonionellina.labradorica* and *Elphidium* spp.). The foraminifera were collected from eight modern coretops close to the Swedish coast from Hanö bay in the Baltic Sea to Skagerrak. In order to examine the accuracy of the produced calibration equations, an attempt was made to reconstruct temperature and salinity conditions in Lomma Bay. This was done by analysing the Mg/Ca in *B.marginata* and *Elphidium* spp. specimens from a core retrieved there and using the calibration equations to estimate past temperature and salinity.

The produced calibration equations showed R^2 values for temperature ranging from 0.1 to 0.5 and from 0.05 to 0.99 for salinity. R^2 values from a multiple regression anlysis conducted on the data ranges from 0.11 to 1.00. The small number of data points resulted in low p-values for all examined taxa, this in combination with a lack of correspondance between estimated values for Lomma Bay temperature and salinity and actual modern values indicates that the calibration equations are not reliable.

Large variations in Mg/Ca are observed ranging from 0.5 mmol/mol (*G.turgida*) to 1.6 mmol/mol (*N.labradorica*). Theese large variations occur over narrow gradients in temperature and salinity indicating that theese variations are mainly due to vital effects.

My thesis contributes to increased knowledge of the distribution of Mg/Ca within benthic species of foraminifera and will contribute to increased knowledge of how Mg/Ca varies due to temperature and salinity in estuarine areas .

Keywords:: Foraminifera, Mg/Ca, temperature, salinity, calibration equations

Supervisor: Helena Filipsson

Subject: Quaternary Geology

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En studie över Mg/Ca i bentiska foraminiferer provtagna över en stor salinitetsgradient

JOHAN GABRIELSSON

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Sammanfattning: Ett flertal studier har funnit ett samband mellan Mg/Ca i foraminiferer och olika miljöfaktorer såsom temperatur (e.g Billups and Schrag, 2002; Dissard et al., 2010; Ferguson et al., 2008). Detta har möjliggjort paleomiljörekonstruktioner baserade på Mg/Ca i foraminiferer. Detta examensarbete har haft som mål att undersöka påverkan av temperatur och salinitet på Mg/Ca i tre arter och ett släkte av bottenlevande foraminiferer (*Bulimina.marginata*, *Globobulimina.turgida*, *Nonionellina.labradorica* och *Elphidium* spp.). Foraminifererna samlades in från åtta moderna kärntoppar i en transekt från Hanöbukten i Östersjön till Skagerrak. För att undersöka precisionen på kalibreringskurvorna som producerats, gjordes ett försök att rekonstruera temperatur och salinitetsförhållanden i Lommabukten på svenska västkusten. Detta gjordes genom att analysera Mg/Ca i *B.marginata* och *Elphidium* spp. Prover- tagna från en kärna provtagen i Lommabukten. De producerade kalibreringsekvationerna användes sedan för att uppskatta tidigare temperaturer och salinitetsnivåer.

De producerade kalibreringsekvationerna uppvisade R^2 värden för temperatur uppskattningarna på mellan 0,1 och 0,5. För salinitet uppvisades R^2 värden på mellan 0.05 och 0.99. R^2 värden på från multipel regressionsanalys uppvisade värden mellan 0,11 och 1,00. Det låga antalet datapunkter resulterade i låga p-värden för alla undersökta släkten. Detta, i kombination med bristen på överenstämmelse mellan de uppskattade värdena för temperatur och salinitet i Lommabukten, och de där uppmäta moderna värdena, indikerar att kalibreringsekvationerna inte är pålitliga.

Stora variationer i Mg/Ca inom de undersökta arterna kan observeras på mellan 0,5 mmol/mol (*G. turgida*) till 1.6 mmol/mol (*N. labradorica*). Dessa stora variationer har observerats över låga gradienter i temperatur och salinitet vilket indikerar att dessa variationer huvudsakligen beror på vitala effekter.

Mitt arbete bidrar till ökad kunskap om hur Mg/Ca fördelas mellan olika bottenlevande foraminiferarter och kommer att bidra till ökad förståelse om hur Mg/Ca varierar med avseende på temperatur och salthalt i kustnära områden.

Nyckelord: Foraminiferer, Mg/Ca, temperatur, salinitet, kalibreringsekvationer

Handledare: Helena Filipsson

Ämnesinriktning: Kvartärgeologi

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1 Introduction

The environmental state of the Baltic Sea is currently affected by multiple stressors including eutrophication and higher $CO₂$ levels, environmental toxins, overfishing, increased temperatures etc. (Duarte et al., 2008). The expected increase in global temperature and changes in multiple climate patterns associated with this will likely put further pressure on the Baltic Sea and Skagerrak. These changing conditions are likely to have a significant effect both on people living in the area and on industries dependent on the Baltic Sea´s ecology, e.g. fishing (Mackenzie et al., 2007). The changing climatic conditions are likely to change the properties of the Baltic Sea in numerous ways e.g. salinity and temperature (Mackenzie et al., 2007), thus changing the basis of the current ecology. In order to understand how the current and future anthropogenic forcings are and will affect the Baltic Seas properties it is imperative to understand how it has reacted to changing circumstances in the past and how the ecology has responded to these changes.

Marine sediments accumulate gradually as material that is transported from land to the ocean or that are formed within the ocean, is deposited. Depending on the location the degree of this sedimentation can vary substantially. While this deposition occurs various marine microorganisms such as diatoms and foraminifera are also deposited. Since these microorganisms are affected by the environmental conditions under which they live studying them can provide information about the environmental conditions that prevailed when they were alive. Marine sediment cores that could potentially contain important information about past climatic and environmental conditions in the Baltic Sea were collected during the IODP Baltic expedition (Andrén et al., 2012). By extracting foraminifera from core tops it is possible to see how modern foraminifera are affected by environmental conditions and this information can then be used to extrapolate backwards. Important information that could potentially be gained from these cores are past sea water temperatures and past levels of salinity. Since different species react differently to changes in environmental conditions it is of great value to have calibration curves which are specific to the species that will be studied. My thesis aims to achieve these goals by creating calibration curves based on how the Mg/ Ca in modern benthic foraminifera collected as part of the DISCO and CONTEMPORARY projects is affected by various environmental conditions. Once calibration curves have been created they will be used to infer paleotemperatures in Lomma bay, SW Sweden.

The Mg/Ca ratio in foraminifera tests is a common proxy for reconstruction of paleotemperatures

(Nurnberg et al., 1996) Due to thermodynamic effects it can be expected that Mg/Ca will follow an exponential curve (Rosenthal et al., 1997) . The Mg/Ca ratio has also been shown to be affected by salinity levels in modern foraminifera (Ferguson et al., 2008) as well as other factors such as carbonate ion concentration (Dissard et al., 2010a). My study has two aims; first to examine how the Mg/Ca ratio in modern foraminifera of the species *Bulimina marginata*, *Elphidium* spp., *Globobulimina turgida* and *Nonionellina labradorica* are affected by environmental salinity and temperature. The second purpose is to apply this data to foraminifera contained in a core from the Lomma bay.

1.1 Foraminifera

Foraminifera are single celled organisms that exist in a wide range of marine settings across the globe. Foraminifera can be divided into benthic and planktonic species with the benthic variety being far more common (around 4000 species) compared to 40-50 known planktonic species. The benthic foraminifera are found in the fossil record as early as the Cambrian while planktonic are not found until the Jurassic (Sen Gupta., 1999). Foraminifera are distinguished by their tests (shells) which are divided into four main groups based on test composition. The four main groups are 1) test composed of organic material, 2) test composed of foreign particles, 3) test composed of calcium carbonate and 4) test composed of silica. All foraminifera used in my thesis belong to the third group with tests composed of calcium carbonate, these can be further divided into low and high Mg species with all foraminifera used in my thesis belonging to the low Mg group. Foraminifera have a broad range of uses in research including temperature and salinity reconstruction (Sen Gupta., 1999) as well as uses in the oil industry for basin analysis (Jones., 2014).

1.1.1 Processes affecting Mg/Ca in foraminifera

Depending on the species the Mg/Ca ratio in foraminifera can vary significantly from levels as low as 0.1 mmol/mol to some with levels of up to 20 mmol/mol (Bentov and Erez., 2006). Hintz et al. (2006a) used culturing experiments to show that large variations in Mg/Ca can occur between foraminifera grown under identical environmental circumstances thus indicating that vital effects have a large impact on foraminifera Mg/Ca (Hintz et al., 2006b). It has also been shown that foraminifera at different stages of development have varying levels of Mg/Ca (Hintz et al., 2006a), with the early and late chambers showing lower Mg/ Ca than middle chambers. Calcifying foraminifera can be divided according to their test structure into hyaline species, that form low Mg calcite (with exceptions) and Miliolids, that form high Mg calcite depending on their test structure (de Nooijer et al., 2009). All foraminifera used in my thesis belong to the hyaline group.

Hyaline foraminifera initiate formation of new chambers by forming a primary organic sheet (POS). The POS has the shape of the new chamber, within this sheet vesicles with an elevated pH are formed and transported to the point of calcification. This process is completed within a matter of hours (de Nooijer et al., 2009). However some dispute that this process is responsible for forming tests arguing that the process is not sufficiently swift for tests to be constructed. Instead it is argued that tests are constructed by a process combining trans membrane transportation and passive transport to new chambers (Nehrke et al., 2013). While incorporation of Mg is also affected by temperature in inorganic calcite the relationship is different in foraminifera. The reasons for this is poorly understood (Bentov & Erez., 2006)

1.1.2 Temperature and salinity

Mg/Ca in foraminifera is widely used in reconstructing past temperature levels (Billups & Schrag., 2002) and the relationship between the two elements has been shown to be affected by temperatures in both modern oceans (Lear et al., 2002) and culturing experiments (von Langen et al., 2005). Several studies have however also found a link between salinity and Mg/Ca in Foraminifera. This has been shown both on benthic foraminifera (Dissard et al., 2010b) and planktonic foraminifera e.g. (Ferguson et al., 2008; Kisakurek et al., 2008). The link has also been shown by both culture experiments (Dissard et al., 2010b; Kisakurek et al., 2008) and in field collected specimens (Ferguson et al., 2008).

1.1.3 Calibration equations

Calibration equations were determined to find the relation between one or several environmental variables and Mg/Ca. By establishing relationships between the environmental variables and Mg/Ca it is possible to determine past salinity and temperature by analyzing Mg/Ca. While the Mg content in inorganic calcite changes due to variations in water Mg content and temperature, calcite formed by living organisms integrate Mg differently (Morse et al., 2007). Extensive literature exists showing that the effects of various environmental variables on Mg/Ca are different both between species and depending on the size of a specimen (Wit et al., 2012). Therefore it has been proposed that species specific calibration curves are the most

precise (Rosenthal et al., 1997). In order to make the calibration equation as precise as possible an attempt was made to narrow the time interval during which the calcite was formed. Filipsson et al. (2004) show that the stable oxygen composition of foraminifera from Swedish fjords were mainly affected by spring temperatures indicating that this is the period when the main calcification occurs. The temperature and salinity values used for the regression analysis in my thesis are therefore the average of March, April, May and June.

1.2 Sampling areas and hydrography

The sampling areas for modern foraminifera studied in my thesis include Skagerrak (including Gullmarfjorden), Kattegat, Öresund and the Baltic Sea (Arkona Basin and Hanö Bay). The sampling points stretch across approximately 375 km on a north to south axis and across 260 km on an east to west axis. Average annual bottom water temperatures ranges from 5.4°C (Hanö bay, CHa-2) to 9°C (Öresund, DV-2) while average annual salinity ranges from 14.9 psu (Hanö bay, CHa-2) to 35.2 psu (Skagerrak, DÅ17). For the location of all sampling points used in my thesis see (Figure 1 and Table 1). The Baltic Sea is connected to the North Sea through the Kattegat and the Danish straits. The Baltic itself can be divided into the Baltic Proper as well as the Gulf of Finland and The Gulf of Bothnia. The Baltic Sea sample points used in this investigation are all from the southern part of the Baltic proper. Due to the large inflow of freshwater from areas around the Baltic Sea, there is net flow of low salinity surface waters into the Kattegat (Winsor et al., 2001).

1.2.1 Skagerrak

Skagerrak´s geographical extent is defined in the west as a line joining $(57°07'N, 8°36'E)$ and $(58°N, 7°E)$ (Fig.1). In the south it is defined by the northern limit of Kattegat (Limits of Oceans and Seas, 1953). Circulation in Skagerrak forms a cyclonic gyre. Water from the North Atlantic and North Sea enters Skagerrak, mainly below the surface along the slopes of the Norwegian trench. This water has a stable salinity of 35 or higher. The surface circulation is strongly affected by wind driven circulation. Outflowing water from the Baltic follows the Swedish coast and leaves the Baltic as the Norwegian Costal Current (Rodhe., 1996). One

Table 1: Coordinates and sampling depth for the various stations included in this study.

Figure 1: Map of sampling localities included in my thesis. Modified from Google Earth 2014.

of the sampling locations used was located in Skagerrak, DÅ17 (58°16.30´ N, 10°30.49´ E).

1.2.2 Kattegat

The geographical extent of Kattegat is defined to the north as a line from Skagen (northernmost point of Denmark) with $(57°54'N, 11°27'E)$ (Fig.1). The line continuous to the northeast through the shoals of Tjörn, north of Gothenburg on the Swedish west coast. To the south it is defined as the limit of the Baltic Sea in Öresund and the Danish straits (Limits of Oceans and Seas, 1953). It covers an area of 22000 $km²$, the depth varies from 50-100 m in the eastern

parts to only 10-20 m in the western parts with an average depth for the entire sea of 23 meters (Gustafsson., 2000) . The hydrography of the Kattegat is dominated by flows between the Baltic and Skagerrak. Low salinity water originating in the Baltic flows to the north along the surface while higher salinity waters from Skagerrak flows in a southerly direction along the bottom. A halocline is typically found at depths between 10 and 20 meters with waters above the halocline showing salinity variations in the range of 15-30 and water below the halocline showing salinity varying between 30 and 35. The temperature meanwhile varies between 4 and 11 °C at 37-40 meters

depth. Water flows into and out from Kattegat is dependent on drainage from the Baltic (Svansson, 1984). Three of the sampling points used in my thesis are located in the Kattegat, DP-2-1 (57°51.95['] N, 11° 18.0´E), DA-1 (57°16.6´ N, 11°25.37´E) and DAn-1 (56°40.13´N, 12°7.0´E).

1.2.3 Öresund and Lomma Bay

Öresund is a strait located between Scania and Denmark (Fig.1). Its border to the Baltic Sea is defined as a line connecting land at 55°17´N, 12°27´E with land at 55°23´N, 12°49´E. One of the sampling points used in my thesis is located in the Öresund, DV (55° 55.59^{γ}N, 12°42.66 γ E). In addition to this, Lomma Bay is located within the Öresund strait and the core was collected here at (55°44,575´N,12°52,881´E). The strait was developed during the deglaciation when the Baltic Ice Lake drained through at Öresund 12600- 12000 ¹⁴Cyr BP. This resulted in the water eroding down to the bedrock (Björck., 1995).

1.2.4 The Baltic Sea

The Baltic Sea has a surface area of $4.2x10^5$ km² and the drainage basin covers $1.7x10^6$ km². It can be divided into several basins generally separated by sills of various depths. Basins include the Bothnian Basin, the Bothnian Sea, the Gulf of Finland as well as the eastern and western Gotland Basins. The basins included in my thesis are the Arkona Basin and the Bornholm Basin. There is no significant sill between these two basins but there are sills separating the Arkona Basin from the Skagerrak, The Darss Sill (18 meters deep) in the Fehrman Belt and the Drogden Sill (8 meters depth) in Öresund. The Baltic Sea has an annual freshwater surplus of 481 km^3 which is mainly from runoff, this excess freshwater leaves the Baltic through the Fehrmann Belt and Öresund with saltier water entering through the same conduits. The brackish Baltic Sea water leaves in the surface layer while higher salinity water enters along the bottom. At irregular intervals significant additional inflows of saline water occurs. Due to the contrast between the Brackish surface layer and the high salinity bottom water the central Baltic Sea is stratified with no ventilation of the bottom waters. In the western Baltic Sea circulation is mainly influenced by the exchange of water with the North Sea. Currents in the Baltic are mostly caused by winds while other factors include water level runoff and fresh water runoff.

1.2.4.1 Arkona Basin

The Arkona Basin is part of the Baltic proper and makes up the southwestern part of the Baltic Sea (Fig.1). The station DBY-2 (55° 00.0´ N, 14°4.95´E) is located in the Arkona Basin.

1.2.4.2 Hanö Bay

Hanö Bay is located outside the eastern coast of Sweden and is part of the Bornholm Basin (Fig.1). The geographical extent of Hanö Bay is limited by the coastlines of the Swedish regions Blekinge and Scania, it has a maximum depth of 60 meters (Nationalatlas., 1992). The station DCHa-2 was located in the Hanö Bay, during 2012 the bottom water temperature varied between a high of 7.16 °C in January and a low of 5.84 °C in November. During the same time the salinity varied between a high of 16.2 in January and a low of 14.0 in December. One of the sampling stations is located in Hanö Bay, Cha at (55°37.6´ N, 14°50.0´ E).

2. Methods

In order to create the desired calibration curves, foraminifera picked from core tops collected as part of the DISCO and CONTEMPORARY projects were analyzed using an optical emission spectrometer at the University of Bremen in Bremen, Germany between the 24 and 28 March 2014. In order to increase the number of data points the data has been combined with Mg/Ca, temperature and salinity data from previously published studies.

2.1 cores

2.1.1 Core from Lomma Bay

The core from Lomma Bay was retrieved by the ship r/ v Sabella using a Gemax corer, on the 11 March 2013. The core was collected at a depth of 21 m at site LN21. CTD measurements of temperature, salinity (indicated by conductivity) and depth was made. Water pressure, current speed and current direction was measured as well. These measurements were made every five meters at the time of core collection and the core was described on site immediately after collection. After the initial collection the core was prepared at the sediment lab at Geocentrum in Lund. The core was sliced into one centimeter thick sections, each section was weighed, freeze dried and weighed again. Mollusc shells were collected from the core in order to allow for AMS 14 C dating. The shells were found in the 13-14 cm interval and the 29-30 cm interval respectively.

2.1.2 Other cores

The modern core tops used in the project were collected as part of the Disco project from nine separate locations described in more detail in the introduction. CTD measurements were made during retrieval. The core tops were stained using Rose Bengal in order to indicate which foraminifera were alive at the time of collection. All samples were sieved using 1 mm, 100 µm and 63 µm sieves, once sieving was complete the individual fractions were dried and each fraction was weighed.

2.2 Dating

Mollusc shells of *Macoma baltica* collected from the Lomma Bay core were sent to the Lund University Radiocarbon Dating Laboratory for dating. The amounts of material used for dating were 1.6 and 4.7 mg of carbon respectively. The resulting 14 C ages were then calibrated in Oxcal (Bronk., 2009) using the Marine13 calibration curve (Reimer et al., 2013) for the mollusc in the 29-30 cm interval and the Bomb(13 NH1) (Hua et al., 2013) curve for the mollusc in the 13 -14 cm interval. A reservoir age of 389 years was used for the lower shell based on Heier- Nielsen et al. (1995). This reservoir age gave a delta R of 22 ± 54 years. A constant rate of deposition was assumed throughout the time since the mollusc shell was deposited.

2.3 Foraminifera identification

Bulimina marginata, Elphidium spp, *Globobulimina turgida* and *Nonionellina labradorica* were picked from the dried samples by hand, using a microscope and a fine paintbrush (for assistance). Only whole foraminifera were picked and when possible uniform size was desired. In the modern cores foraminifera that were alive during the sample collection (as indicated by rose Bengal) were selected. Among the *Elphidium* spp specimens the majority consisted of *Elphidium excavatum* but small numbers of *Elphidium albiumbilicatum* and *Elphidium incertum* were also included

2.4 Mg/Ca measurements

Mg/Ca preparation and measurements were made at the University of Bremen in Bremen, Germany between the 24 and 28 March 2014. The foraminifera were cleaned before measurements were conducted in order to remove any potential contamination such as clay and organic material. The number of B.*marginata* specimens from DÅ17 were sufficient to allow for two separate samples to be measured. The cleaning method was a modified version of the one laid out by (Barker et al., 2003). The cleaning procedure was as follows:

1. Before cleaning commenced the specimens were crushed between two glass plates in order to open up all chambers. The ease with which the foraminifera were crushed was noted as it indicates how well they were preserved. Once the crushing was completed the material was transferred to a vial and water was added (Figure 2).

2. In order to remove clay from the material 500 µl of water was added to each vial. Air bubbles were removed by gently tapping the glass. Superfluous water was then removed using a pipette and the vials

were placed in an ultrasonic bath at ten percent of the baths effect for two minutes. 500 µl of water was then added again, air bubbles were removed and superfluous water was removed. This step was repeated four times. Once cleaning with water was completed 250 µl of analytical grade methanol was added to the vials and the vials were placed in an ultrasonic bath for two minutes. Once the vials were removed from the ultrasonic bath the superfluous methanol was removed. This procedure was repeated one more time. 500 µl of water was then added and removed to remove the methanol.

3. In order to remove organic material from the sample an oxidation step was included. A solution of 250 µl alkali buffered 1% H₂O₂ and 25 ml of 0.1 M NaOH was prepared. 250 µl of the solution was then added to each vial. The vials were then placed in warm water for a total of ten minutes. Every two minutes and 30 seconds the vials were removed and tapped in order to remove air bubbles. After five and ten minutes in the water bath the vials were placed in the ultrasonic bath for a short duration of time. Once the procedure was completed the solution was removed. This procedure was repeated two times. The samples were then washed by adding and removing 500 µl of water three times.

4. The final cleaning stage was an acid leach. The samples were transferred to new vials and 250 µl of 0.001 M HNO₃ was added to each vial. The samples were then transferred to the ultrasonic bath and left for 30 seconds. Once removed from the ultrasonic bath the acid was removed and 500 µl of water was added and removed, the water addition and removal was then repeated (Figure 2).

5. After the acid leach was completed the material was dissolved. As much solution as possible was removed before the dissolution of remaining material

Figure 2: Selected procedures used during Mg/Ca measurements. Clockwise from top: crushing of foraminifera, acid leach, ultrasonic bath, warm water bath, centrifuge and the ICP-OES.

commenced. Once this was done 500 µl of 0.075 M HNO3 was added and the sample was placed in the ultrasonic bath until the entire sample was dissolved. Once the dissolution was completed the sample was placed in a centrifuge (6000 rounds per minute) for ten minutes (Figure 2).

6. Before measurements the samples were diluted, in order to achieve an optimal amount of Calcium in the samples (10-80 ppm Ca). The extent of dilution varied depending on the amount of material that was remaining.

7. The measurements were conducted using an Inductively Coupled Plasma-Optical Emission spectrometer (ICP-OES) (Figure 2).

2.5 Data treatment

The resulting values for the Mg/Ca data and environmental conditions as well as data from previous investigations were plotted in a scatterplot in Excel, and an exponential trend line was fitted to the data points yielding an exponential equation for the values. In order to examine to which degree a combination of the various factors could explain variations in the Mg/Ca ratio a multiple linear regression analysis was made on the data with the R^2 value indicating the degree of explanation and p-vales used to indicate the accuracy.

3 Results

3.1 Dating

The mollusc shells were dated using AMS-14C to 108.9± 0.8 pMC at the 13-14 cm level and to 650± 45 years B.P at the 29-30 cm level. The calibrated age for the mollusc shell in the 29-30 cm level was between 1528 and 1787 cal. years B.P with an average value of 1644±116 cal. years A.D. The calibrated age for the mollusc shell found in the 13-14 cm level was determined to be from either $1956-57$ or $1997-2004 \text{ A} \text{ D}$. (Either side of the bomb peak). In order to calculate the deposition time the depth of the highest date was divided by its age. If the older of theese two dates is assumed to be correct it would result in an annual deposition rate of 0.23 cm per year.

3.2 CTD data at location Lomma and DISCO

CTD (conductivity, temperature and depth) plots were made during the retrieval of both the core taken from Lomma Bay and for the cores retrieved as part of the DISCO project. The DISCO project had access to a more advanced CTD allowing for more accurate measurements. For full plots see appendix I

3.3 Species distribution data

Of the four species that were used one, *Bulimina marginata* was found at five locations and the other three were found at three locations. In the core from Lomma Bay only two species were examined (*Bulimina marginata* and *Elphidium* spp).

3.3.1 *Bulimina marginata*

Bulimina marginata was found alive in five of the modern sampling sites (DÅ17, DF-1d, DAn-1c, DV-1c and DA-1c) as well as dead in the Lomma Bay core. The specimens from the modern core tops were generally well preserved, based on how difficult they were to crush. In the Lomma Bay core the specimens were collected from the top layer down to 6 cm in the core. The specimens from Lomma Bay were easily crushed indicating that they were in a worse state of preservation. In the modern core tops there were more than 20 specimens in all samples while it was necessary to merge the samples from Lomma Bay into three samples in order to obtain a large enough mass.

3.3.2 *Elphidium* spp.

Elphidium spp. was found alive in three of the modern sampling sites (DBY-2, Dcha-2b and Dv-1c) as well as dead in the Lomma Bay core. In the modern core tops the preservation state was reasonably good while the preservation state was poor to moderately good in the Lomma Bay core, again based on ease of crushing. As with B. *marginata* more than 20 specimens were found in all modern core tops while it was necessary to merge several levels in the Lomma Bay core. Despite this, however, some samples were still close to the minimum amount that can be reliably analyzed using an optical spectrometer.

3.3.3 *Globobulimina turgida*

Globobulimina turgida was found in three of the modern sampling sites (Da-1c, DV-1c and DAn-1c). Based on ease of crushing the preservation state was poor to moderately good. Only one of the localities contained more than 20 specimens. However the other two still yielded enough material to exceed the minimum level required for accurate measurements by the spectrometer.

3.3.4 Nonionellina labradorica

Nonionellina labradorica was found in three of the modern sampling sites (DAn-1c, DV-1c and DP2B). The crushing of the specimens indicated moderately good to good preservation. Two of the samples contained more than 20 specimens while the third was still above the necessary amount of material.

| Species | Sample | Station | Ca (ppm) | Mg/Ca (mmol/mol) | Avr. Ca (ppm) | Avr. Mg/Ca (mmol/mol) |
|--------------------------|----------------|--------------------|----------|---------------------|---------------|--------------------------|
| Bulimina | | DÅ17- | | | 32.256 | 2.281 |
| Marginata | J1 | 1 _b 1 | 53.31 | 2.253 | | |
| | J2 | DÅ17- 1b2 | 54.31 | 2.215 | | |
| | J3 | $DF-1d$ | 42.17 | 1.663 | | |
| | J4 | DAn-1c | 27.19 | 2.058 | | |
| | J5 | $DV-1c$ | 28.19 | 2.262 | | |
| | J ₆ | $DA-1c$ | 16.94 | 2.402 | | |
| | | LN21c | | | | |
| | J18 | $0 - 1$ | 7.446 | 3.884 | | |
| | | LN21c | | | | |
| | J19 | $2 - 4$ | 28.35 | 2.023 | | |
| | | LN21c | | | | |
| Elphidium spp. | J20 | $4 - 6$ $DBY2-$ | 32.4 | 1.775 | 18.386 | 1.492 |
| | J7 | 1A | 27.94 | 1.395 | | |
| | ${\rm J}8$ | Dcha-2b | 17.66 | 0.817 | | |
| | J9 | $DV-1c$ | 21.74 | 1.584 | | |
| | | Ln21c | | | | |
| | J10 | $0 - 1$ | 26.94 | 1.54 | | |
| | | LN21c | | | | |
| | J11 | $1 - 2$ | 10.63 | 3.503 | | |
| | | LN21c | | | | |
| | J12 | $2 - 3$ LN21c | 5.664 | 1.029 | | |
| | J13 | $3-4$ | 30.95 | 1.586 | | |
| | | LN21c | | | | |
| | J14 | $4 - 5$ | 21.25 | 1.326 | | |
| | | LN21c | | | | |
| | J15 | $5 - 7$ | 11.92 | 1.124 | | |
| | J16 | LN21c $7 - 9$ | 18.09 | 1.282 | | |
| | | LN21c | | | | |
| | J17 | $9 - 11$ | 9.457 | 1.222 | | |
| Globobulimina turgida | J24 | $DA-Ic$ | 14.42 | 1.848 | 16.46 | 1.894 |
| | J25 | $DV-1c$ | 11.19 | 1.67 | | |
| | J26 | DAn-1c | 23.77 | 2.165 | | |
| Nonionellina | J21 | DAn-1c | | | 57.48 | 2.449 |
| labradorica | | | 99.71 | 2.058 | | |
| | J22 | $DV-1c$ | 47.07 | 1.857 | | |
| | J23 | DP2B | 25.66 | 3.432 | | |

Table 2. Ca concentration and Mg/Ca values for the samples. Samples with calcium concentration outside of the optimal span are marked red

3.4 Mg/Ca data

The Mg/Ca content varied from a low of 0.817 mmol/ mol to a high of 3.884 mmol/mol (Table 2), for complete data see Appendix II. In order for the machine to take accurate readings it was necessary to have a calcium concentration of between 10 and 80 ppm in the samples. All of the *Globobulimina turgida* samples were within this range as were all the modern samples

of *Bulimina marginata* and *Elphidium* spp. One of the modern *Nonionellina labradorica* samples exceeded the maximum level. Among the samples taken from Lomma Bay one of the B. *marginata* and two of the *Elphidium* spp. samples were below the minimum level for accurate readings.

3.5 Calibration curves

3.5.1 *Bulimina marginata*

The *B. marginata* calibration equation is based on measurements on specimens from five core tops collected as part of the Disco project as well as data from four samples described in (Groeneveld & Filipsson., 2013). Data on temperature and salinity as well as Mg/ Ca was fed into an Excel spreadsheet and displayed in a scatterplot (Figures 3, 4). An exponential trend line was fitted to the data points that can be described by the function Mg/Ca=1.3031e^{0.078T} with an R² value of 0.1 for the temperature and $Mg/Ca=0.0979e^{0.0888S}$ with an R^2 value of 0.05 for the salinity. In order to correct for the two variables both affecting Mg/Ca a multiple linear regression analysis taking into account both variables was made to find the combined R^2 value of the two variables. For *B. marginata* this value equals 0.11 with a p-value of 0.93 meaning that only just above 10% of the change in Mg/Ca ratio can be explained by changes in temperature and salinity. The low R^2 values indicate that only a small fraction of the change in Mg/ Ca can be explained by changes in temperature, salinity or the two combined.

3.5.2 *Elphidium* spp.

The *Elphidium* calibration equation is based on measurements conducted on specimens from three modern

Fig. 3: Mg/Ca values of *Bulimina marginata* as related to temperature.

Fig 4: Mg/Ca values of *Bulimina marginata* as related to salinity.

core tops as well as values from two cultured samples of *Elphidium williamsoni* used in a culturing experiment by (Allison et al., 2010). The data was treated in the same way as the data from the *B. marginata* samples and yielded calibration curves that can be described with the function $Mg/Ca=0.5049e^{0.445T}$ with an R^2 value of 0.5 for temperature and Mg/ Ca= $0.6907e^{0.0287S}$ with an R² value of 0.64 for the salinity (Figure 5,6). The higher R^2 value for temperature and the fact that DV-1 has a relatively low Mg/Ca value despite salinity levels above 30 indicate that temperature is the dominant control on Mg/Ca. As with the *B*. *marginata* samples the R^2 value from a multiple linear regression analysis was used in order to find to what extent the Mg/Ca ratio was affected by a combination of changes in temperature and salinity. This yielded an R^2 value of 0.73 with a p-value of 0.36 meaning that 73 percent of the change in Mg/Ca ratio can be explained by changes in salinity and temperature.

3.5.3 *Globobulimina turgida*

The *G. turgida* calibration curve is based on data from three samples analyzed as part of my thesis and from

Fig 5: Mg/Ca for *Elphidium* spp. as related to temperature.

Fig 6: Mg/Ca for *Elphidium* spp. as related to salinity.

four measurements conducted by Groeneveld & Filipsson (2013). The data was treated in the same way as above and yielded calibration curves described by the function Mg/Ca = $3*10^{-5}e^{0.3306S}$ with an R² value of 0.17 for the salinity and $Mg/Ca=0.4656e^{0.2751T}$ with an

 $R²$ value of 0.15 for the temperature (Figures 7, 8). The similar R^2 values indicates that temperature and salinity both have an equal effect on Mg/Ca. The R^2 value for the combined temperature and salinity is 0.31 with a p value of 0.13.

3.5.4 *Nonionellina labradorica*

The *Nonionellina labradorica* calibration curve is based on specimens from three samples analyzed as part of my thesis. The data was treated in the same way as it was for the above three species. The resulting calibration curves can be described by the functions Mg/Ca= $8*10^{-14}$ e^{0.8981S} with an R² value of 0.99 for salinity and Mg/Ca= $0.4213e^{0.2727T}$ with an R² value of 0.10 for temperature (Figure 9, 10). The R^2 value from the multiple linear regression equals one indicating that all of the difference in Mg/Ca can be attributed to changes in temperature and salinity. However, there were to few data points to calculate the p-value.

Fig 7: Mg/Ca for *Globobulimina turgida* as related to temperature. Note the large error bar on the first measurement in this study.

Fig 8: Mg/Ca for *Globobulimina turgida* as related to salinity.

3.6 Estimates for Lomma Bay

3.6.1 Estimates based on *B.marginata*

Using the calibration equations it was attempted to estimate the temperature in Lomma Bay based on the three *Bulimina* samples from Lomma that were meas-

ured. This resulted in values of salinity ranging from 32.6 to 41 and values of temperature varied from 14 to 4° C (Table 3).

3.6.2 Estimates based on *Elphidium* spp.

The calibration equations above were implemented on *Elphidium* samples from Lomma Bay in order to estimate past temperature and salinity levels. The resulting values ranged from 13.9 to 56.5 for salinity and from 1.4 to 29°C for the temperature (Table 4).

Fig 9: Mg/Ca for *Nonionellina labradorica* as related to temperature

Fig 10: Mg/Ca for *Nonionellina labradorica* as related to salinity.

4. Discussion

4.1 Calibration equations

Thermodynamic effects indicates that Mg/Ca will follow an exponential curve (Rosenthal et al., 1997) accordingly an exponential curve was fitted to the data. However, there are also claims that this relationship is linear (Farmer et al., 2012). When using multiple regression, a linear correlation was assumed in order to simplify data treatment.

4.1.1 *Bulimina marginata*

The results show that virtually no effect exists on the Mg/Ca ratio that can be attributed to changes in temperature this contradicts numerous previous studies that have found a clear relationship between the Mg/

Ca ratio and temperature in *B. marginata* (Wit et al., 2012). The limited effect of temperature on Mg/Ca is unexpected because of the significant amount of literature that shows a relationship between foraminifera Mg/Ca and temperature. One possible explanation of this may be that variation in other environmental factors overshadowed the effects of temperature and salinity. However the existence of large Mg/Ca variations between the samples of 1.19 mmol/mol across small temperature and salinity gradients at 1.45°C and 0.95 respectively could be interpreted as the species natural variation and not due to environmental factors. This variation would be significant compared to several other studies, Kristjansdottir et al. (2007) found Mg/ Ca ratios varying with 0.45, 0.45 and 1.57 mmol/mol over a temperature gradient of 7°C. Billups & Schrag (2002) found a variation in Mg/Ca of 1.13 mmol/mol over a temperature gradient of 3.62°C. However other studies have found significant variations in Mg/Ca over relatively narrow temperature gradients. Rathburn & De Deckker (1997) found a variation in Mg/Ca of 2.93 over a temperature gradient of 2.11°C.

4.1.2 *Elphidium* spp.

Varekamp (2004),unpublished but found in (McGann., 2008), determined a logarithmic calibration equation based on *Elphidium excavatum* from the Long Island Sound, USA . The calibration equation; water temperature= 4.4289 ln(Mg/Ca)+ 11.682 differs substantially from the one that results from plotting the data in my thesis; water temperature = $6.5333 \ln(Mg/Ca)$ + 4.3134

(Figure 5). This difference could be attributed to different factors, one possible explanation is that the different localities could potentially result in differences in various other environmental factors that influenced the curves. A second explanation could be that while Varekamp (2004) only included *Elphidium excavatum* the curve in my thesis also relied on values from *Elphidium incertum* and *E. albiumblicatum* as well as data from Alison et al. (2010) that is based on *Elphidium williamsoni*. If the data from Alison et al. (2010) is not included in order to reduce these sources of error the calibration curve changes significantly and the R^2 values for temperature and salinity falls to 0.01 and 0.42 respectively. The *Elphidium* samples analyzed as part of my thesis were retrieved from areas with large differences in salinity. However, there is no corresponding increase in the Mg/Ca value. Salinity increases by 18.94 between the DBY-2 station and the DV station however in the samples from these two stations Mg/Ca increases by only 0.18 mmol/mol. Meanwhile salinity increases by 0.22 between Cha-2 and DBY-2 while Mg/Ca increases by 0.58. This indicates that for *Elphidium spp.* salinity plays a limited or no role at all in the Mg/Ca content.

4.1.3 *Globobulimina turgida*

Carbonate ion concentration could possibly explain part of this difference in Mg/Ca, as could variations in oxygen concentration (Groeneveld & Filipsson, 2013). The temperature equation can be compared to the calibration equation developed by Skinner et al. (2003) for *G. affinis* which is a different species but of the same

Table 4: Estimated temperature and salinity in Lomma Bay core based on the *Elphidium* calibration equation

genus. The calibration equation is $Mg/Ca=2.91e^{0.08T}$ with an R^2 value of 0.93. This varies significantly from the calibration equation found that is based on data from the DISCO project and Groenveld & Filipsson (2013). However, the difference can likely be attributed to the significant differences in circumstances with the calibration equation developed by Skinner et al. (2003), it being on a different species under colder environmental conditions. The difference in Mg/Ca between the highest and lowest samples were 3.29 mmol/mol across salinity and temperature gradients of 0.85 and 1.13°C, respectively. This large variation across narrow gradients combined with low R^2 values indicate that a large part of the variation can be explained by vital effects rather than environmental conditions.

4.1.4 *Nonionellina labradorica*

While the R^2 values for salinity and from the multiple linear regression analysis are very strong only three datapoints are included. Due to the low number of datapoints no p-values could be calculated, because of this the data can be seen as highly uncertain. Further, changes in both temperature and salinity are very small with changes of only 0.68°C and 0.85 respectively. For these reasons it is highly uncertain if changes in Mg/Ca are due to environmental factors or due to vital effects.

4.2 Paleo conditions in Lomma Bay

The calibration equations created from modern samples were applied to the foraminifera from the Lomma Bay core. The deposition rate was calculated to 0.23 cm/year. However, this rate of deposition relies on the assumption that the oldest date for the top dating is correct. If the younger date would be correct it would indicate an annual rate of deposition closer to 1 cm/ year, this value appears unrealistic. The average deposition rate in the area (as seen from the difference in age and depth between the two dating points) was calculated to between 0.03 cm/year and 0.09 cm/year. This indicates that the assumed deposition rate is either to high or accelerated markedly towards the top of the core. Further complicating this is the effect of mollusc burrowing which would result in the mollusc used for dating being younger than the surrounding sediments, the large difference between average deposition rate and the deposition rate in the top layer indicates that burrowing has compromised the results. The magnitude of this effect is hard to quantify, however.

4.2.1 Paleo conditions in Lomma Bay based on *B. marginata*

The estimated values for salinity are higher than the values observed during sampling (Table 3) but are close to those found in the present day Öresund bottom waters (with the exception of the top point). The temperature values are also higher than those during sampling and are lower than the values found in present day bottom waters (with the exception of the top point).

4.2.2 Paleo conditions in Lomma Bay based on *Elphidium* spp

With the exception of the 1974-1983 sample the temperature values were not close to the modern ones. The average estimated temperature of 6.5°C (excludes the 2004-2009 sample) is close to the modern levels in Öresund. The salinity level was with the exception of the 2004-2009 interval far lower than the modern lev-

Fig 11: Estimated palaeotemprature in the Lomma Bay core based on *Elphidium* spp. and *Bulimina marginata*. Data for *Elphidium* spp. is based on the calibration equation developed as part of my thesis (purple line) and on a calibration curve by Varenkamp (green line). Data for *B. marginata* is based on the calibration curve developed as part of my thesis (blue line) and on the calibration equation presented in Wit et al. (2012)(red line).

els. There can be multiple reasons for why the 2004- 2009 sample showed a markedly different result than the other measurements. One possible explanation is that the calcium concentration in the sample (10.63 ppm) was very close to the lower limit required for accurate readings (10 ppm). Another possible explanation could be that other environmental factors affected the Mg/Ca in this specific sample. However Alison et al. (2010) examined how the Mg/Ca values in *Elphidium williamsoni* was affected by changes in pH and carbonate ion concentration. They found no correlation which would indicate that these factors are not the reason for the high values.

4.2.3 Comparison of estimated Lomma values based on *Bulimina marginata* and *Elphidium* spp.

Due to a sometimes too low number of specimens it was not possible to sample at the same intervals for *Bulimina marginata* and *Elphidium* spp. Therefore the two records are not fully comparable. The Mg/Ca values varied significantly between the two species with

Fig 12: Estimated variation in palaeosalinity in the Lomma Bay core based on *Elphidium* spp.(red line) and *B. marginata* (blue line).

an average value of 1.58 mmol/mol for *Elphidium* spp. and 2.56 for *B. marginata*. This difference is maintained at all levels except during 2004-2009 where Mg/Ca in the *Elphidium* spp. sample exceeded the value in *B. marginata* (Figure 11). However this relationship also held true at the modern sampling point (DV in Öresund) where both species were found. Here *B. marginata* had a value of 2.26 mmol/mol and *Elphidium* spp. had a value of 1.58. This indicates that *B. marginata* has higher values of Mg than *Elphidium* spp. naturally either because of the way they build their shells or because of different blooming periods. Since the 2009-2011 sample for B. *marginata* and the 2004-2009 interval for *Elphidium* spp. are clear outliers comparing the top two centimeters would likely be misleading. However, at lower levels it is possible to compare the two species. During 1996-2009 B. *marginata* displays a temperature of 5.6 degrees while *Elphidium* averages 6.3 degrees between 1996 and 2009. In order to compare how the calibration equations in my thesis compares to other calibration equations the results for paleotemperatures based on the calibration equation in my thesis were plotted against results based on the calibration equation produced by Varekamp (*Elphidium* spp.) and Wit et al. (2012) (*B. marginata*). Both of these equations demonstrate higher temperatures that seem unrealistic (Figure 11). Salinity varies substantially, however, with *B. marginata* having a value of 35.03 psu in the same interval, while *Elphidium* spp. shows an average value of 17.4 psu Compared to modern observed temperature and salinity values (from CTD at retrieval site and measuring in Öresund) B. *marginata* displays realistic values for salinity (Figure 12), while the values for temperature are bellow the modern day values. The values based on the *Elphidium* spp. calibration equation produces values that are generally lower than present day for salinity. The temperature values vary significantly with an average close to modern day temperatures. The difference in estimated values can be due to multiple reasons including different calcification periods,

different reactions to factors not estimated and deficiencies in one or both of the calibration curves.

4.3 Potential sources of error

Apart from the data treatment there are multiple sources of error that have the potential to compromise the results. These sources occur during the entire process from errors in the individual specimens and picking of the specimens to the measurements. The sources of error occurring before the data treatment are described below

4.3.1Rose Bengal

Rose Bengal was used to determine which specimens were alive during sampling and could thus be considered to represent recent levels of temperature and salinity. However Rose Bengal can be considered to serve as a source of error in to ways;

1. The entire test was not always colored while a complete or almost complete coloration was strived for. This means that, to some extent, subjective selection occurred.

2. Bernhard et al. (2006) show that foraminifera which were colored were often found to not be alive at the time of coloring. This is because Bengal rose reacts with organic matter which is not always the same as those foraminifera that are alive. This would indicate that more foraminifera are determined to be alive than actually is. The precise extent of this error source is unknown but on average it has been found that only half of the foraminifera dyed by Rose Bengal are actually alive (Bernhard et al., 2006). However the potential effect of this source of error is limited due to the relatively low year to year variations in temperature and salinity that occurs at the sampling points

4.3.2 Clay contamination

Clay contamination would be an indication of incomplete cleaning and would influence the Mg/Ca. Due to the four most common minerals in marine sediments containing between 1 and 10 wt% Mg (Deer et al., 1992) it is imperative to remove the largest possible amount of these clays if accurate measurements are to be made. A step of the cleaning procedure was dedicated to removing this contamination and in order to examine whether this was successful the Mg/Ca was plotted against the Al/Ca. A linear relationship between the two would indicate that the samples are contaminated (Barker et al. 2003). However only a weak relationship can be observed (Figure 13) with an \mathbb{R}^2 value of just 0.09 indicating that the cleaning was successful.

4.3.3 Low salinity/temperature gradients

With the exception of *Elphidium spp.* all three species that were examined were deposited in areas that had narrow gradients in salinity and temperature. This means that the effects on the Mg/Ca that may be due to one or both of the examined variables may be "camouflaged" or enhanced by changes in other variables working in the opposite direction.

4.3.4 Differences between species

A large number of studies indicate that substantial differences in the Mg/Ca occur between different species (e.g. Hintz et al., 2006). Since the *Elphidium* samples are comprised of multiple species of the same genus this effect could have a large impact on the accuracy of the *Elphidium* calibration curve. However since the majority of specimens from the DISCO project are of the species *Elphidium excavatum* this effect is most likely relatively small (on these samples). The specimens from Alison et al. (2010) have Mg/Ca values that are above the trend line for the DISCO samples. However this could to some extent be explained by the fact that both temperature and salinity was higher in the culture study.

4.3.5 Differences between individual tests

There exists large variations in Mg/Ca values between different tests of the same species, collected from the same location (Wit et al., 2012). Since the measurements were made on multiple specimens simultaneously it is difficult to estimate to which extent this affected the results but it is possible to narrow this uncertainty to some degree. One major contributor to

Fig 13: Relationship between Mg/Ca and Al/Ca in all meassured samples.

variations in the Mg/Ca between individual specimens is their variation in size (Anand & Elderfield, 2003). In order to minimize the effect of this it was attempted to pick foraminifera as uniform in size as possible wherever possible. Secondly, in a larger sample size variations tend to cancel each other out. While these two factors do not completely rule out errors due to indi-

vidual differences it can be said with a reasonable degree of certainty that it likely did not cause any significant effect errors in the salinity and temperature estimates.

5 Conclusions

- The produced calibration equations are not of sufficient accuracy to be used for paleo environmental reconstructions. This is attributed to low temperature and salinity gradients combined with too few measuring points.
- The included *B. marginata* samples showed large variations over small salinity and temperature gradients. This combined with low R^2 values means that no reliable calibration equations can be established. The significant variations in Mg/Ca can likely be attributed to vital effects.
- Mg/Ca in *Elphidium* spp. seems to be unaffected by changes in salinity levels. The samples collected as part of my thesis does a strong correlation with temperature. However the small number of data points means that it cannot be concluded that there is a correlation.
- As with *B. marginata*, *G. turgida* shows large variations in Mg/Ca over limited salinity and temperature gradients combined with low R^2 values for the calibration equations.
- While calibration equations for *N. labradorica* show high R^2 values for salinity and strong correlation when both temperature and salinity are considered, the small number of data points and very narrow temperature and salinity gradients make these equations unreliable.
- Significant variations in Mg/Ca across narrow gradients in both temperature and salinity can be observed in *B.marginata, G.turgida* and *N.labradorica*. These variations can likely be attributed to vital effects and can be seen as a source of error in temperature and salinity reconstructions based on these species.
- In order to create more accurate calibration equations it is necessary to obtain additional data points with larger variations in temperature and salinity.

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Data som används i uppsatsen är hämtade från SMHIs databas SHARK (Svenskt HavsARKiv). Data har tagits fram inom svensk samordnad miljöövervakning av Bohuskustens Vattenvårdsförbund, Hallands Kustkontrollprogram, Öresunds Vattenvårdsförbund, Sydkustens Vattenvårdsförbund och Vattenvårdsförbundet för västra Hanöbukten.

Appendix I

Figure 14:CTD profiles from Stations used in my thesis collected as part of the DISCO project. In order from top stations; DÅ17-1, DA-1, DP-2, Dan-1, DV, Cha, DBY-2 and DF-1. From R/V Skagerrak cruise repport collected 4 -12 November 2013.

Figure 15: CTD profile from station LN21C on March 11 2013.

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