Variability of freshwater reservoir effects
Implications for radiocarbon dating of prehistoric pottery and organisms from estuarine environments

PhD thesis

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Chapter 1

Introduction

This PhD project is located in the intersection of physics and archaeology, extending into palaeo-environmental research, and might be called an interdisciplinary project. Having received professional training both in physics and archaeology, I am in the lucky position to be a specialist in both fields, and am thus able to carry out an interdisciplinary study on my own.

As Grahame Clark noted, in interdisciplinary research, the “co-operation between specialists must be genuine, that is to say that specialists must maintain their integrity” (Clark, 1981). I have done my best to keep the thesis at a high scientific level for both disciplines. At the same time, I have tried to explain the physical and archaeological concepts in a way that they might be understandable for specialists from the respective other discipline. I hope my readers, no matter what their scientific background may be, will find the level of this thesis appropriate and will forgive me for any over-simplified or over-complicated explanations.

Some of the research for this PhD project had already been initiated in my Diploma (master’s) project. Some preliminary results can be found there (Philippsen, 2008). As neither the principles of radiocarbon dating nor the character of the sites and cultures analysed have changed, readers who are familiar with my previous work might spot a few repetitions.

The general assumption in radiocarbon dating is that the dated sample had been in equilibrium with the atmosphere so that its initial radiocarbon concentration is known. The lower the measured radiocarbon concentration compared to the initial concentration, the older the sample. However, there are reservoirs with lower radiocarbon levels than the atmosphere. These include the oceans and freshwater systems like lakes and rivers. Samples originating from these reservoirs have low radiocarbon concentrations to begin with. A freshly caught fish can thus be measured to be a thousand years old! This age deviation is called reservoir age, and the effect that causes it, marine reservoir effect or freshwater reservoir effect. The marine reservoir effect is a well-known and fairly well understood phenomenon. Radiocarbon ages of samples from the open seas around Denmark, for example, can be corrected by subtracting 400 years. The freshwater reservoir effect, in contrast, is elusive, complex and variable in time and space, as this study will illustrate.

1.1 Motivation

This study began with one research question, which evolved into a variety of investigations. The question was, is the earliest pottery found in Northern Germany really that old?

The age of pottery from inland sites was determined by radiocarbon dating of charred food remains on the sherds, the so-called food crusts. The result was an archaeological sensation. This Stone Age pottery was not only found to be the oldest ever dated in this region, as old as 5400 BC, but also to be almost a thousand years older than pottery from coastal settlements of the same culture. How could inland groups be a thousand years ahead of their fellows on the coast, less than 100 kilometres away?

Maybe a reservoir effect could explain the high ages – the inland sites with old pottery were at rivers, so a freshwater reservoir effect was suspected. But how large is the freshwater reservoir effect in these rivers? Could it really explain the sensationally high radiocarbon ages of the pottery? Radiocarbon dating of fish bones and contemporaneous “terrestrial” samples such as wood should give the answer – the reservoir age
CHAPTER 1. INTRODUCTION

would just be the difference of radiocarbon ages of these two sample types. However, it was difficult to find clearly associated aquatic and terrestrial samples at these sites.

Therefore, I tried to quantify the modern freshwater reservoir effect in that region, its order of magnitude and degree of variability. Water, aquatic plants and animals were radiocarbon dated and found to be up to several thousand years old. A substantial reservoir effect in these rivers in the Stone Age is therefore likely.

However, the presence of “old fish” in a river does not automatically cause high ages in the pottery used next to it. A high age would obviously only be transferred to the food crusts on pottery if fish had been cooked in these pots.

Consequently, the pottery itself was analysed to find the ingredients which had formed the food crusts. The potential of different methods such as stable isotope analysis, infrared spectroscopy and lipid analysis was explored. For these methods, as well as for radiocarbon dating, reference samples were produced by replicating the prehistoric production of pottery, as well as cooking and scorching of food.

The freshwater reservoir effect was found to be large and highly variable from one season to the next, and between different organisms from the same river. This lead to further questions: How large is reservoir effect variability over large time-scales, and to which degree does the freshwater reservoir effect influence radiocarbon dating in an estuarine environment? Can we just assume a marine reservoir effect and subtract 400 years from the radiocarbon dates of fish bones, shells and people who had lived on marine resources from the Limfjord, for example? Or does the freshwater reservoir effect disturb radiocarbon dating in this environment, too?

In order to answer this question, terrestrial macrofossils and mollusk shells from a sediment core in the Limfjord were radiocarbon dated, and the reservoir age was calculated for the period 7300 to 1300 cal BP. Furthermore, stable isotopes of the sediment were measured in order to identify the origin of the organic matter. These measurements contributed to a multi-proxy study in which the development of the Limfjord was investigated.

Food crusts on pottery and samples from a sediment core can be very small compared to routine radiocarbon samples. Therefore, some improvements for the preparation of small samples were suggested and tested, especially for combustion and graphitisation.

1.2 Structure

In chapter 2, I explain the natural sciences concepts that are required for understanding this study. These are of course the measurement techniques, mainly radiocarbon dating and stable isotope analysis, but also excursions into other disciplines, e.g. freshwater botany or infrared spectroscopy. The freshwater reservoir effect is a complex phenomenon, and chapter 2 reflects this complexity. For understanding how the freshwater reservoir effect works, for example, we have to understand how carbonates are dissolved in groundwater, or how aquatic plants photosynthesize. I cannot go into depth for all aspects of neighbouring disciplines, but will provide the information that I use for the analysis of my measurements in chapters 6 and 7 as well as references for the interested reader.

Chapter 3 presents the specific methods and parameters chosen. Some aspects of these methods are attempted to be improved in chapter 4, as small samples, such as food crusts on pottery, pose challenges especially during combustion and graphitisation.

Radiocarbon dating and stable isotope measurements, in combination with other techniques, are applied in two case studies of reservoir effects. One focuses on radiocarbon dating of the earliest Stone Age pottery in Northern Germany and short-term variability of freshwater reservoir effects in this region (chapter 6). The other examines the long-term variability of reservoir effects in the Limfjord in Northern Denmark, which is influenced by both freshwater and marine reservoir effects (chapter 7). Chapter 5 provides the environmental and cultural background for the two case studies.

A short conclusion, chapter 8, sums up the main results of chapter 4, 6 and 7. The appendix contains an overview over graphite cathodes prepared for chapter 4, and a reference library of FTIR spectra of food crusts on pottery which was prepared during the pottery studies in chapter 6.

Many of the results from chapter 6 and 7 have been (or will be) published in several articles. These are included in the list of publications.
1.3 List of publications

1.3.1 Peer-reviewed publications


Bente Philippsen and Jan Heinemeier (in press) “Ertebølle Cuisine: A freshwater radiocarbon reservoir effect in Mesolithic food crusts from Northern Germany.” Food and Drink in Archaeology

Bente Philippsen, Jesper Olsen, Jonathan P. Lewis, Peter Rasmussen, David B. Ryves, Karen Luise Knudsen (submitted) “Mid- to late-Holocene reservoir age variability and isotope-based palaeoenvironmental reconstruction in the Limfjord, Denmark” The Holocene

Bente Philippsen, Oliver Craig, Carl Heron, Sönke Hartz, Katerina Glykou, John Meadows, Jan Heinemeier (in preparation) “Radiocarbon dating prehistoric pottery from Northern Europe” Radiocarbon

Bente Philippsen and Jan Heinemeier (in preparation) “Freshwater reservoir effect variability in Northern Germany” Radiocarbon

Jonathan P. Lewis, David B. Ryves, Peter Rasmussen, Karen L. Knudsen, Kaj S. Petersen, Jesper Olsen, Melanie J. Leng, Peter Kristensen, Suzanne McGowan, and Bente Philippsen (submitted) “Environmental change in the Limfjord, Denmark (ca. 5,500 BC-AD 500): a multiproxy study” QSR

1.3.2 Other scientific publications


1.3.3 Popular science publications


CHAPTER 1. INTRODUCTION

1.4 Acknowledgments

This study would not have been possible without the major and minor contributions of numerous people, and I would like to express my sincere thanks to all of them.

My main supervisor Jan Heinemeier and my supervisor Jesper Olsen gave me the opportunity to work with the interesting topics described in this thesis. The whole AMS $^{14}$C group, including former staff and students, helped me with remarkable patience whenever I needed assistance.

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My co-authors of the manuscripts listed above taught me a lot about their fields of expertise while we were writing and discussing together.

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Dorte Spangsmark and Linda B. Madsen from Aalborg University in Esbjerg measured the fatty acid composition of lipids absorbed in potsherds and food crusts. Oliver Craig from the University of York and Val Steele from the University of Bradford extracted lipids from pottery for radiocarbon dating. Karl Georgsen from the Department of Chemistry, Aarhus University, helped me with the preparation of these samples. Erik Thomsen and Hans Dieter Zimmermann from the Department of Geoscience, Aarhus University, taught me how to use the petrographic microscope.

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Chapter 2
General Background and Methodology

This section describes the general background of the techniques used in this study. Specific information about my measurements can be found in chapter 3. The first part of this chapter is dedicated to \(^{14}\)C dating. The method will be presented, and reservoir effects will be explained. Then, stable isotope \((^{13}\text{C}, ^{15}\text{N}, ^{18}\text{O})\) analyses will be introduced and illustrated with several applications, especially from archaeology. Finally, some additional methods for the analysis of prehistoric pottery will be presented. One of them, lipid analysis, is widely used for ceramics and yields interesting results. The other three additional methods are widely used in archaeological science for several materials, but have not been established as methods for pottery analysis. The applicability of these methods will be discussed. The results will be presented in chapter 6.

The first two sections in this chapter deal with the measurement of isotopic ratios, either of radioactive or of stable isotopes. The name “isotope” consists of the Greek words \textit{isos}=equal and \textit{topos}=place, because isotopes of an element are situated at the same position of the periodic table of elements. All isotopes of an element have the same number of protons and electrons. They have thus similar chemical properties. The isotopes of an element differ only in their number of neutrons, i.e. their masses. The \(^{13}\text{C}\) atom is for example 8\% heavier than \(^{12}\text{C}\), whereas \(^{14}\text{C}\) is 17\% heavier than \(^{12}\text{C}\) (Browman, 1981). The mass differences can change diffusion rates, because heavier isotopes are not as mobile as lighter ones. The mass difference between isotopes also leads to different reaction rates, because heavier isotopes have higher binding energies, so their bindings are more stable.

“Isotopic fractionation” is the enrichment of a certain isotope of an element. The extent of fractionation caused by isotopes of a certain element is the greater the smaller the molecules are that contain this isotope. Fractionation between the different carbon isotopes, for example, is large when \(\text{CO}_2\) diffuses into leaves, but is smaller for the transport of photosynthesis products like sucrose \(\text{C}_{12}\text{H}_{22}\text{O}_{11}\), where the exchange of one carbon atom with another isotope does not affect the relative molecular mass so strongly. In this study, the abundances of the stable and radioactive carbon isotopes \(^{13}\text{C}\) and \(^{14}\text{C}\), and of the stable nitrogen and oxygen isotopes \(^{15}\text{N}\) and \(^{18}\text{O}\) are measured and compared to the abundances of the lighter, most numerous isotope: \(^{14}\text{C}/^{12}\text{C}, ^{13}\text{C}/^{12}\text{C}, ^{15}\text{N}/^{14}\text{N}\) and \(^{18}\text{O}/^{16}\text{O}\).

2.1 Radiocarbon dating

Radiocarbon dating is an absolute dating method and has been used for about 70 years.

Both in archaeology and geology, relative dating methods have a long tradition. They are either based on stratigraphy (the oldest artefacts/formations usually lie deepest), or on type fossils, e.g. a certain pottery style or a certain life form that occurred during a limited period of time. Gradual changes in artefact style can be used in archaeology to construct typological sequences for relative dating. However, often absolute dating is necessary, as relative dating cannot answer all questions. One example is the calculation of the length of certain cultural phenomena. Also for comparison of environmental proxies from different sites in geology, absolute dating is needed. Finally, in archaeology, the spread of innovations like pottery, agricultural techniques or monumental constructions can only be unravelled when the phenomena are absolutely dated in the different areas.

Radiocarbon dating is based on the fact that there is a nearly constant concentration of \(^{14}\text{C}\) in atmospheric \(\text{CO}_2\), due to the equilibrium between radioactive decay and production by cosmic rays. Plants incorporate this \(\text{CO}_2\) through photosynthesis, animals and humans by consumption of plants or animals. At the death of the organism, the uptake of \(^{14}\text{C}\) ends and the \(^{14}\text{C}\) in the dead plant or animal decreases according to the exponential decay law (Figure 2.1,
ganism, uptake of $^{14}\text{C}$ carbon isotope development from the discovery of the radioactive principles of radiocarbon dating. I will illustrate the I have chosen a historical perspective to explain the

2.1.1 Historical development of $^{14}\text{C}$ radiocarbon dating

Figure 2.1: While alive, all organisms have a nearly constant $^{14}\text{C}$ concentration. At the death of the organism, uptake of $^{14}\text{C}$ ends and the $^{14}\text{C}$ concentration decreases according to the exponential decay law, with a half-life of 5730 years.

equation 2.1). For calculating the age of a sample, its $^{14}\text{C}$ concentration $A$ is measured and is compared to the $^{14}\text{C}$ concentration of the atmosphere at the time when the organism was alive, $A_0$:

$$A = A_0 e^{-t/\tau} \text{ with } \tau = 8267a.$$  (2.1)

As the atmospheric $^{14}\text{C}$ concentration is not completely constant, a so-called calibration curve is needed for calculating a calendar age from the measured radiocarbon age. In the calibration curve, the radiocarbon ages of tree rings are plotted against their dendrochronologically determined calendar ages. This calibration curve is used for the conversion of $^{14}\text{C}$ ages to calendar ages, or “calibrated ages”.

2.1.1 Historical development of radiocarbon dating

I have chosen a historical perspective to explain the principles of radiocarbon dating. I will illustrate the development from the discovery of the radioactive carbon isotope $^{14}\text{C}$ to the routine measurements of today. Some of the basic assumptions of the early days have proven inaccurate. However, this has always led to new knowledge and made the method even more reliable. The information presented in this section has been extracted from the articles in Taylor et al. (1992), when not indicated otherwise.

Two key points lead to the state of knowledge which provided the basis for $^{14}\text{C}$ dating. On the one hand, the unstable $^{14}\text{C}$ carbon isotope was discovered in 1937 (Ruben and Kamen, 1941). It was observed that $^{14}\text{C}$ was produced by cosmic rays which provide free neutrons in the atmosphere:

$$^1\text{n} + ^{14}\text{N} \rightarrow ^{14}\text{C} + ^1\text{p}$$  (2.2)

and that $^{14}\text{C}$ decays to nitrogen:

$$^{14}\text{C} \rightarrow e^- + ^{14}\text{N} + \bar{\nu}_e.$$  (2.3)

$^{14}\text{C}$ was found to have a half-life “between 1,000 and 25,000 years”, thus corresponding to archaeological time scales (Korff and Danforth, 1939). Later, the half-life was determined more precisely to 5568 years, which was used for the first datings. Even though the half-life was not known exactly, the theoretical knowledge about the $^{14}\text{C}$ atom and its decay was hence available in the 1940s. On the other hand, Willard Libby had invented the screen-wall counter. The practical basis was consequently also given. This counter measured radioactivity and was thus capable of measuring the number of decaying $^{14}\text{C}$ atoms, the activity of a sample.

The first list of radiocarbon ages for unknown samples was published in 1951 (Arnold and Libby, 1951) after the idea had been proposed by Willard Libby in 1946. The first radiocarbon laboratory in Europe was established in Copenhagen, Denmark, in 1951, after Hilde Levi had learnt about the method on a study trip to the USA in 1947-48. In the summer of 1952, the first unknown samples were dated (Anderson et al., 1953). The introduction of radiocarbon dating is often called the first radiocarbon revolution and earned W. Libby the Nobel Prize in chemistry in 1960. The first radiocarbon measurements were analyzed using a mean life of 8033 years or half life of 5568 years, called Libby’s mean life and half life. It is still used, for example when an age is stated as $^{14}\text{C}$ years BP. In 1960, more precise measurements gave a half life of 5730 years and, correspondingly, a mean life of $\tau = 8267$ years. The conversion between half life and mean life can be understood when regarding the decay law (identical to equation 2.3) with the activity of the sample after time $t$, $A$, and its original activity, $A_0$:

$$A = A_0 e^{-t/\tau} \text{ with } \tau = 8267a.$$  

After the half life, by definition, the activity is halved:

$$0.5 = 1 e^{-t_1/\tau} \rightarrow \ln \frac{1}{2} = -\frac{t_1/2}{\tau} \rightarrow \tau \ln 2 = t_{1/2}.$$  

The NBS (National Bureau of Standards, USA) established oxalic acid as a standard to which archaeological samples are compared (Browman, 1981).
2.1. RADIOCARBON DATING

The leader of the USGS (US Geological Survey) Radiocarbon Dating Laboratory, Hans E. Suess, became famous for the discovery of the “Suess effect”, the anthropogenic drop in $^{14}\text{C}$ activity in air which occurred during the industrial revolution, when $^{14}\text{C}$-free CO$_2$ from fossil-fuel combustion was added to the atmosphere. This drop in atmospheric $^{14}\text{C}$ concentration is one of the reasons for the fact that the initial $^{14}\text{C}$ concentration of a sample in the past is not the same as the “present” atmospheric $^{14}\text{C}$ concentration.

In 1959, de Vries demonstrated the variability of atmospheric $^{14}\text{C}$ over the past centuries. The variations in $^{14}\text{C}$ level are called “wiggles”. It took a long time until the existence of those wiggles were widely accepted, and still they are not fully understood. The long-term variations in the $^{14}\text{C}$ production rate are caused by variations in the geomagnetic field intensity, the short term variations are caused by the heliomagnetic modulation of $^{14}\text{C}$ production (Browman, 1981). Also the Earth’s climate has an influence on the atmospheric $^{14}\text{C}$ concentration. When the global temperature decreases, the partial pressure of CO$_2$ in the atmosphere decreases so that the specific $^{14}\text{C}$ concentration is one of the reasons for the fact that the initial $^{14}\text{C}$ concentration of a sample in the past is not the same as the “present” atmospheric $^{14}\text{C}$ concentration.

Dendrochronology provides samples of a known age for testing radiocarbon dating (e.g. Christensen, 2007). When $^{14}\text{C}$-dating a tree ring of known age, one can therefore calculate the atmospheric $^{14}\text{C}$ activity of the time when the tree ring was formed. When this is done for a long stretch of time reaching back in the past, one can give the initial $^{14}\text{C}$ activity for each year. The plot of this information is called the calibration curve, as it can be used for calibrating a measured $^{14}\text{C}$ concentration to obtain a calendar age. A multitude of calibration curves was produced in the following years. In August 1979, an International Calibration Committee was formed to solve the problems of different calibration curves. Still, in 1981 there were more than 14 different curves. The free-hand curve drawing through the data points, which was common at that time, also lead to different calibration curves even if the data were the same (Browman, 1981). Regardless of all disagreements, the introduction of calibration and the re-interpretation of datings was perceived as the second radiocarbon revolution. Today, participants of the international Radiocarbon conferences agree on a new version of the terrestrial and marine calibration curves every three years. The calibration curve used for most calibrations in this study is IntCal09 (Figure 2.2 Reimer et al., 2009). The effect of calibration on the uncertainty of the calibrated age is illustrated in figure 2.3. A plateau in the calibration curve leads to very broad probability distributions of the calibrated age between 800 and 400 cal BC, the period of the Hallstatt culture. The uncertainty of the calibrated age depends thus also on the shape of the calibration curve, and not only on the uncertainty of the $^{14}\text{C}$ measurement.

During these first decades, radiocarbon dating was performed by decay counting. Only the $^{14}\text{C}$ atoms decaying during the measurement period could be detected. The sample masses required for this technique were about 1 g carbon (1 gC). Not all types of samples could be dated: The carbon yield of different sample materials differs a lot, so that in some cases far more than only few grams of original sample were needed. Very small samples could thus not be dated. Other samples are too valuable for allowing the removal of for example 100 g sample material to obtain the required 1 gC. In a modern sample, the average fraction of $^{14}\text{C}$ decaying per day equals only $2.4 \cdot 10^{-7}$ of the amount present (the half-life of radiocarbon is 5730a, so when in 5730a 50% of the $^{14}\text{C}$ atoms decay, in one day, $0.5/5730/365=2.4 \cdot 10^{-7}$ of the $^{14}\text{C}$ atoms present will decay). If the number of $^{14}\text{C}$ atoms present could be counted directly, the sample size could be reduced drastically. The most important background in decay counting, the cosmic radiation, would also be eliminated (Kirner et al., 1995).

The direct counting of $^{14}\text{C}$ atoms is possible with accelerator mass spectrometry (AMS). It is in principle a very easy technique: The carbon atoms are extracted as ions from the sample, they are accelerated, separated from each other, and counted. The separation and counting of isotopes of different masses is called mass spectrometry. Accelerator mass spectrometry is a mass spectrometric measurement with the help of an accelerator. All mass spectrometers accelerate ions to a few keV to dominate over the spread in energy of the ions emitted from an ion source, but the accelerator is needed for $^{14}\text{C}$ dating to exclude mass ambiguities by destroying molecular ions (Litherland et al., 1987).

In 1977, two independent approaches using particle accelerators were taken, one with a cyclotron and one with a tandem Van de Graaff electrostatic accelerator. In May 1977, $^{14}\text{C}$ in an organic sample (barbecue charcoal) was measured via AMS for the first time. The team at the University of Rochester (USA) demonstrated that negative $^{14}\text{N}$ ions are unstable (Gove, 1992). Thus, the most important dis-
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Figure 2.2: The terrestrial calibration curve IntCal09, after Reimer et al. (2009). Black line = mean, area shaded green = 1σ.

For these first attempts of AMS radiocarbon dating, existing accelerators were used. Later, small tandem accelerators were specifically designed for AMS, because the high terminal voltages of the big accelerators were not necessary. All that was required was a negative ion energy high enough to have a reasonable probability of producing charge 3+ ions in the terminal stripper to ensure the elimination of mass 14 molecules. At the end of the 1970s, $^{14}C$ was measured with completely acceptable sensitivity using small tandem accelerators with terminal voltages around 2 MV.

As the sample size could be reduced to about 1/1000, a whole new range of samples became datable. A reduction of sample mass in conventional measurements, the use of small-counter facilities, had the disadvantage of long measurement times: several days for one sample. AMS with measurement times about half an hour to a few hours per sample is thus much more effective. The small required sample mass makes it possible to date objects that were too small or too valuable to be dated with the conventional method. When e.g. a bone is reasonably well preserved, $^{14}C$ dating and stable isotope analysis is possible without destroying the object (Arneborg et al., 1999). Therefore, the introduction of AMS is also termed the third radiocarbon revolution (Tuniz et al., 2003). Especially when dating the introduction
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Figure 2.3: A section of the calibration curve “IntCal09” displaying the calibration of 50 fictional radiocarbon samples. These are assumed to have calendar ages equally distributed between 1500 and 520 cal BC and are indicated by tick marks on the calendar age axis. Their $^{14}$C age is determined using the calibration curve. Each $^{14}$C age calibrated applying an uncertainty of 30 $^{14}$C years. Note the plateau in the calibration curve which leads to broad probability distributions of calibrated/calendar ages during the Hallstatt period (800-475 cal BC). Figure by Jesper Olsen.
of agriculture in different areas, AMS is the only possible dating method that can directly date the key material, single cereal grains. Those plant remains are too small to be dated conventionally and too mobile to be dated stratigraphically or via associated finds (Harris et al., 1987). AMS samples are not only smaller, but also more easily prepared than samples for decay counting. All three carbon isotopes can be accelerated. In principle, both the date from $^{14}$C/$^{12}$C or $^{14}$C/$^{13}$C as well as additional information from $^{13}$C/$^{12}$C is available.

It is possible to measure other radionuclides beyond $^{14}$C with the accelerator. Long-lived cosmo-genic radioisotopes can be detected in the presence of vastly larger quantities of their stable isotopes (Tuniz et al., 2003). Many radionuclides which are produced in measurable amounts in the atmosphere or environment have decay constants matching temporal scales relevant to the history of hominidae (Tuniz et al., 2003). While $^{14}$C can reach 500,000 years ago, when Homo sapiens sapiens started colonizing vast regions of our planet, $^{10}$Be and others can reach back to 5 million years when Australopithecus appeared. They all can be measured by AMS, although the only cosmogenic radionuclide discussed in this thesis will be $^{14}$C. The different detectable radioisotopes can not only be used for dating. A plenitude of applications in hydrology, geoscience, materials science, biomedicine, sedimentology, environmental sciences and many other fields emerged as soon as the AMS detection capabilities of the appropriate isotopes were demonstrated. One example is the measurement of $^{36}$Cl. It was produced in nuclear weapon tests in the 1950s by neutrons interacting with the chlorine in the seawater. It was injected into the biosphere at a level which was two orders of magnitude above the pre- and postbomb test ambient levels and could be used for measuring water flow rates (Tuniz et al., 2003).

2.1.2 AMS $^{14}$C dating in praxis

A modern sample of 1 g carbon contains $5.8 \cdot 10^{10}$ $^{14}$C atoms. A mass spectrometer for detecting the radioisotope in a modern sample must have a detection limit of the order of $10^{-12}$, whereas dating a 60000 year old sample, which only contains 1/1000 of the initial $^{14}$C, necessitates a resolution of $10^{-15}$ to $10^{-16}$ (Browman, 1981). Additionally, a mass spectrometer for $^{14}$C dating must be able to discriminate between particles of nearly equal mass such as $^{14}$N, $^{14}$C, $^{13}$CH, $^{12}$CH2. The mass of $^{14}$N, for example, differs by only one part in 10⁷ from the mass of $^{14}$C (Browman, 1981). With AMS, it is possible to detect approximately 1% of all $^{14}$C present in a sample. The efficiency of AMS is thus 100 to 1000 times as great the efficiency achieved by decay counting.

Before the measurement, the sample has to be cleaned of contaminants and converted to a form that is measurable with the AMS system. In the following, we will follow a sample from the chemical pre-treatment through target preparation and measurement until the calculation and reporting of a radiocarbon age.

Chemical pre-treatment of the sample

One of the basic assumptions for radiocarbon dating is that the sample, as measured, contains carbon that came only from a living organism or a similar system that ceases to be in chemical exchange with the biosphere after a certain date, which is determined by radiocarbon dating. However, in praxis, the sample can contain contamination, i.e. substances that have a radiocarbon age different from that of the sample. Contamination can to a great extent be removed chemically. Chemical pretreatment isolates and purifies the chemical phase or phases that represent the event or archaeological culture or geologic stratum to be dated (Long, 1992). However, as each additional step in the chemical pre-treatment by itself bears the risk of introducing contamination e.g. from the chemicals or containers used, the pre-treatment procedure should be kept as simple as possible.

Two important classes of contaminants that enter archaeological samples during burial are carbonates and humic substances. Carbonates are transported with soil water and can be incorporated into the mineral fraction of bones, but also into other sample types. They can be removed by acidifying the sample with hydrochloric acid, HCl. Shells are composed of carbonate. Therefore, the amount of HCl for pre-treatment is chosen according to sample size so the outer e.g. 10% are removed, while the rest of the sample is not dissolved.

Humic substances are a fraction of the dissolved organic carbon in soils. The characterization of different humic substances is largely based on separation methods. Humic substances have the relatively high molecular weight in common that can be up to several 100,000 mass units, or several 100kD. They are refractory, heterogenous, alkali soluble and give the dark colour to soil and water (Clark and Fritz, 1997). Humic substances include humic acids, fulvic acids and insoluble humic substances. Humic acids precipitate from solution at pH < 2. Fulvic acid is soluble at all pH values. Both humic and fulvic acid derive from humification of vegetation, for example from cellulose and other carbohydrates, proteins, lignins and
tannins, by bacterial metabolism and oxidation. Humic substances are removed with sodium hydroxide, NaOH, from the samples. This necessitates a final HCl step to remove any atmospheric CO$_2$ which the samples might have absorbed while they were basic.

The general considerations about the removal of carbonates and humic substances described above also apply to bones. However, some additional steps are often incorporated for making sure to isolate the chemical fraction that represents the true age of the bone. Bone and antler consist to approximately one third of organical primary substance, i.e. ossein and fat (Dellbrügge, 2002). Two thirds of the bone consist of inorganic material, carbonate hydroxyapatite (Piotrowska and Goslar, 2002), composed to 85% of calcium phosphate, furthermore containing calcium carbonate and calcium fluoride (Dellbrügge, 2002). On the soil surface and in well-aerated soils such as sand or gravel, bones are not preserved: microbiological processes degrade organical substances and the silicid acid in the sand dissolves mineral substances. In contrast to that, the preservation conditions for bone are excellent in humid sediments from lakes and bogs or in submarine sites. Only in high moors the high acidity (pH as low as 2) dissolves the mineral substances (Dellbrügge, 2002).

Bones have a surface area of about 10 m$^2$ g$^{-1}$. Due to the high porosity, they are very susceptible to contamination. It is expected that the organical substance of the bone changes least during deposition in the soil. Therefore, the bone pretreatment method is protein extraction, or “gelatinisation”. Most laboratories today use a “modified Longin-method”, referring to the paper by Longin (1971). In the original Longin method, the crushed bone is treated with 8% HCl at 20°C for about 20 minutes to remove carbonate and to break some of the hydrogen bonds of the collagen. The collagen is extracted from the residue in an aqueous solution with a pH of 3.0 at 90°C for about 10 hours. Finally, the gelatin solution is dried in an oven. This method has been modified by lowering the temperature to 58°C and introducing ultrafiltration (Brown et al., 1988).

The extracted substance is often referred to as collagen, although it is well known that the degraded bone material is different from the original collagen (Kanstrup, 2008). As bone substance consists in the average of bigger molecules than contaminants from the soil, the extracted dissolved “collagen” is sometimes ultra-filtered to exclude small molecules. Usually, the >30 kDa fraction is used for dating and isotope analysis. The most common type of collagen, Type I, has a molecular mass between 95 and 102 kDa (Piotrowska and Goslar, 2002). Also in “modified Longin-methods”, the first step of the bone preparation is usually an acid treatment at low temperature, 20°C or less. This dissolves the mineral substances of the bone as well as secondary carbonate that was transported into the bone by water (Piotrowska and Goslar, 2002). Another important group of contaminants, the humic substances (see above) can be removed by alkali treatment, but are also excluded during the gelatinisation of the collagen (Piotrowska and Goslar, 2002). The gelatinisation is the treatment of the remaining sample with a weak acid at high temperatures, about 60°C. This dissolves the collagen. The solution is freeze-dried, after optional ultrafiltration. The method used at the Aarhus AMS $^{14}$C Dating Centre, and which I applied to my bone samples, includes gelatinisation and ultra-filtration. Details can be found in section 3.1.3.

The preservation of bone samples can be classified according to the amount of original collagen remaining (Piotrowska and Goslar, 2002, citing Hedges and van Klinken (1992)):

- excellently preserved: >20% of the original collagen remains (<40 mg/g)
- well preserved: 20-5% of collagen (10-40 mg/g)
- poorly preserved: <5% of collagen (<10 mg/g)
- non-collageneous: <0.5% of collagen (<1 mg/g)

Collagen that was extracted with a low collagen yield can still be suitable for dating, but the smaller the yield, the bigger the sample needs to be — and that increases background contamination (Piotrowska and Goslar, 2002). The gelatin (“collagen”) yield can be used as a criterion of the sample’s quality. Bonsall et al. (2004) for example do not routinely date yields below 10 mg collagen per g sample, i.e. samples that are not “well preserved” according to Piotrowska and Goslar (2002) and Hedges and van Klinken (1992). The demands on collagen yield were reduced in newer literature when ultrafiltration was applied, so that a yield of 1 mg collagen per g sample is sufficient for some groups (Kanstrup, 2008). For samples prepared without ultrafiltration, yields above 3.5% (35 mg collagen per g sample) are required. Another criterion for the chemical integrity of the extracted gelatin is the C/N ratio of the bone — if it is inside a certain range, one can be fairly sure that the extracted substance is collagen. Bonsall et al. (2004) define a range of acceptability between 2.9 and 3.6. This range can be refined to between 3.1 and 3.5 for radiocarbon dating (Kanstrup, 2008, and references therein). Also the weight percentages of carbon and nitrogen in the collagen can be used as quality indicators; well-preserved collagen has around 35 wt% carbon and 11 to 16 wt% nitrogen (van Klinken, 1999).
Conversion to CO$_2$

DIC from water and shell carbonate are acidified with phosphoric acid to yield CO$_2$. Organic samples are combusted in evacuated quartz tubes containing CuO, which undergoes pyrolytic decomposition at $>500^\circ$C (Boutton, 1991) and thus provides oxygen for the combustion. The CuO is a significant contribution to contamination. It has often lower carbon concentration than the catalyst for graphitisation (see below), but usually, the amounts of CuO used for one sample preparation are some orders of magnitude larger than the catalyst (Alderliesten et al., 1998).

The samples can also be combusted in an elemental analyzer (EA) at a temperature of 1030$^\circ$C with supply of gaseous oxygen (see figure 2.4). In this process, carbon and nitrogen from the sample are converted to CO$_2$ and N$_2$. The EA is coupled to a stable isotope ratio mass spectrometer (IRMS), where $\delta^{13}$C and $\delta^{15}$N can be measured. In chapter 4, a combination of the combustion for $^{14}$C dating and stable isotope measurements is proposed.

Target preparation

The CO$_2$ from acidification or combustion has to be converted to a form that is measurable with AMS. The method development (chapter 4) focuses on this part of the sample preparation.

For the sputter ion sources used for AMS $^{14}$C measurement, compressed, filamentous graphite is a suitable material (McNichol et al., 1992). The process that reduces the CO$_2$ is commonly called graphitisation, irrespective of the structure of the reduced carbon. The sample CO$_2$ is transferred to the graphitisation system by placing it in a tube cracker, which is evacuated before the tube is broken manually. The CO$_2$ is transferred cryogenically into a calibrated volume, where the CO$_2$ pressure after defreezing can be translated into an equivalent carbon mass, milligram carbon (mgC). The desired quantity of gas, usually 1mgC, is transferred cryogenically into the reaction volume for graphitisation. About 0.2mgC of CO$_2$ are kept in an ampoule for $\delta^{13}$C measurement with the IRMS, as a $\delta^{13}$C measurement is essential for a fractionation correction of the $^{14}$C measurement.

The Aarhus AMS $^{14}$C Dating Centre uses H$_2$ as reductant, the most common method. The zinc reduction method is also feasible, especially after recent improvements (Xu et al., 2007), but will not be discussed here.

The graphitisation process has been studied using various approaches (see e.g. McNichol et al. (1992); Němec et al. (2010) and references therein), but due to the complexity of the reaction and variety in demands from the different AMS systems, an empirical approach finding the optimum graphitisation procedure for each lab is recommended (Turnbull et al., 2010). In some cases, it can thus be complicated to measure the graphite produced in one lab with another lab’s AMS machine. During this study, for example, a new high intensity ion source was installed at the Aarhus AMS system. This required an adaptation of the graphite and cathodes, especially for small samples. A new focus of the investigation in chapter 4 was therefore the preparation of cathodes optimized for the new ion source.

The overall reaction taking place during graphitisation is $\text{CO}_2 + 2\,\text{H}_2 \xrightleftharpoons{\text{W}} \xleftleftharpoons{\text{E}} \text{C} + 2\,\text{H}_2\text{O}$. The equilibrium is shifted towards the right side by cryogenic removal of the water. In reality, though, a multitude of reactions takes place in the reactor, as McNichol et al. (1992) demonstrated by analysing the contents of the graphitisation reactor with a residual gas analyzer:

- $\text{CO}_2 + \text{H}_2 \xrightleftharpoons{\text{W}} \text{CO} + \text{H}_2\text{O}$
- $\text{CO} + 2\,\text{H}_2 \xrightleftharpoons{\text{W}} \text{C(gr)} + \text{H}_2\text{O}$
- $2\,\text{CO} \xrightleftharpoons{\text{W}} 2\,\text{CO}_2 + 2\,\text{C}$
- $2\,\text{CO} + 2\,\text{H}_2 \xrightleftharpoons{\text{W}} 2\,\text{CO}_2 + \text{CH}_4$
- $\text{CO} + 3\,\text{H}_2 \xrightleftharpoons{\text{W}} \text{H}_2\text{O} + 3\,\text{CH}_4$
- $\text{C} + 2\,\text{H}_2 \xrightleftharpoons{\text{W}} \text{CH}_4$

The following graphitisation parameters are used in Aarhus:

- reductant: H$_2$
- catalyst: cobalt or iron powder
- temperature: 500 to 700$^\circ$C

Because of the high temperatures, quartz glass (melting point 1600$^\circ$C) is used for the reaction tubes (“reactors”), as pyrex glass (melting point 600$^\circ$C) could melt or deform. The quartz tubes are stored in a humidified atmosphere prior to graphitisation to reduce problems with static. World-wide, graphitisation temperatures covering a wide range from 200 to 650$^\circ$C are used. Some groups avoid low temperatures because of the production of methane instead of graphite. Interestingly, other groups avoid the very high temperatures for the same reason (Turnbull et al., 2010).

The graphitisation takes place in the presence of a transition-metal catalyst, usually cobalt or iron. A specific type of catalyst from different manufacturers, batches, or even different bottles from the same batch, can perform very differently during graphitisation and AMS measurement (Santos et al., 2007). It is thus common practice to test every new bottle of catalyst and assess its graphitisation characteristics and radiocarbon background levels (Turnbull et al., 2010).

The amount of catalyst, or the graphite-to-catalyst ratio, is an important parameter for AMS measurement. It has to be optimized for each lab to achieve the highest signal and the lowest contamination. The optimal catalyst-to-graphite ratio depends on the type of AMS machine and the quality of the graphite. Generally, a higher concentration of catalyst leads to a higher AMS signal but also increases the risk of contamination.

In summary, the graphitisation process is a crucial step in AMS radiocarbon dating. It transforms organic samples into graphite, which is then used for radiocarbon measurement. The process is complex and can be optimized for each lab to achieve the best results.
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Figure 2.4: From chemically pretreated sample to $\delta^{13}C$, $\delta^{15}N$ and $^{14}C$ results - the method currently used at the Aarhus AMS $^{14}C$ Dating Centre. See text for detailed description. $\delta^{13}C$ (DI) can be left out when $\delta^{13}C$ (EA-CN) is measured. For samples where a $\delta^{15}N$ measurement would not give extra information, like charcoal, the whole tin capsule-EA-CN process is left out.

ratio, also has an influence on sample performance. Large amounts of catalyst should be avoided as the catalyst is a possible source of contamination (Santos et al., 2007).

The catalyst is preconditioned prior to the graphitisation by heating it in the presence of $H_2$. Some groups start the preconditioning with a $O_2$-step. Hua et al. (2004), for example, could reduce the graphitisation time to one third after preconditioning the catalyst with $O_2$. However, this was not considered necessary at the Aarhus AMS centre, also because of the risk that can arise when using $H_2$ and $O_2$ in the same system.

The graphite-catalyst mixture is compressed into a target. This process is called “mounting”. From this target, negatively charged carbon ions are produced by sputtering with caesium. This target is often termed cathode. The usual method that has been used in Aarhus is mounting in aluminium cathodes. A hole is pressed into the cathode and filled with a thin layer of silver. The catalyst-graphite mixture is placed on top of that and covered with a copper foil. Then, the mixture is compacted by pressing gently. The copper foil is removed, and the graphite-catalyst mixture is pushed into the middle of the cathode again. This can be repeated a couple of times before pressing with maximum pressure. The silver powder can also be left out; Alderliesten et al. (1998) for example only used silver powder for the smallest samples.

In chapter 4, different approaches on improving the sample preparation are investigated.

Measurement

All laboratories have their specific design of an AMS setup. I will try to explain the principles as general as possible, but when more details are needed, I will refer to the setup that had been used at the $^{14}C$ AMS dating laboratory at Aarhus University. In summary, the carbon ions are extracted from the sample, accelerated with 0.5-10 MV, separated according to their momentum, charge and energy and finally counted by an ion detector after identification by nuclear mass and charge. The following account is based on Beukens (1992) and pers. comm. by Klaus Bahner and Jan Heinemeier. It is summarized in figure 2.7 (for the mass-14 beam).

The target is placed into the ion source and a beam
of caesium ions is focused onto its surface. This causes negative carbon ions to leave the sample surface. They are accelerated towards a positive electrical potential. The most important mass-14 component that disturbs the $^{14}$C measurement is already removed: $^{14}$N does not form negative ions and is therefore not present in the ion beam. The ion energy is the sum of the energy they obtained from the acceleration towards the positive potential, which is the same for all of them, plus the kinetic energy they obtained from the ionization. Therefore, the ions have different energies. The ion beam is therefore electrostatically deflected, so only ions with the desired energy $E$ are moving on the trajectory of radius $r$:

$$
\varepsilon r = \frac{MV^2}{Q} \propto \frac{E}{Q} \tag{2.4}
$$

with $M =$ nuclear mass, $Q =$ charge, $v =$ velocity and $E =$ kinetic energy ($E = \frac{1}{2}mv^2$) of the ion and $\varepsilon =$ electric field. We have thus obtained a beam of ions with equal energy. Ions with mass 12, 13 and 14 are now selected for injection into the accelerator by a magnetic field in which the ions are deflected according to:

$$
\frac{ME}{Q^2} \propto (Br)^2 \tag{2.5}
$$

with $B =$ magnetic field. Only ions with a specific $ME/Q^2$ are deflected to the circular path with radius $r$. As all ions have the same charge (-1 from the ion source) and as the above-mentioned electrostatical filter had selected ions with equal energy, one can also say that only ions with a specific mass are deflected to the circular path with radius $r$. By varying the magnetic field intensity $B$, one can again choose between the ions with mass 12, 13, or 14. As this magnet is used for injecting beams of ions of different masses, it is called injection magnet. The mass-14 beam consists mainly of $^{12}$CH$_2$ and $^{13}$CH$^-$. $^{14}$C is present in this mass-14 beam, but its percentage is negligible as the other carbon isotopes are far more abundant. The next steps serve to isolate $^{14}$C in the mass-14 beam, beginning with the tandem accelerator (Fig. 2.5). The negative ion is attracted by a positive potential in the middle of the accelerator. Typical acceleration voltages are between 2MV for Tandetrons and 6MV for Van de Graaff accelerators. In the middle of the accelerator, a so-called stripper material is installed. This can be a foil or a gas, such as Argon, which was used in Aarhus. Collisions with the stripper material remove several electrons, so that the resulting carbon ions are positively charged. +3 is the most common case for 2MV acceleration and +4 for 6MV. When losing 3 or more electrons, molecules such as $^{12}$CH$_2$ and $^{13}$CH$^-$ from the mass-14 beam, are not longer stable.

![Figure 2.5](image)

**Figure 2.5:** A negative ion beam enters the tandem accelerator, loses electrons in the stripper material and leaves the accelerator with a charge of 3+.

The stripper removes thus the interfering molecules. As an example, when using an accelerator with 3MV and a charge state of +3, the ions gain an energy of (1+3)-3 MeV = 12 MeV through acceleration with the tandem accelerator on top of the energy $E$ (equation 2.4) from ionization and acceleration out of the ion source (first, the ions in a charge state of -1 are attracted by the positive potential of 3MV, then they are in a charge state of -3 and repelled by the same potential). After the accelerator, another magnetical analysis (after equation 2.5) is necessary: Charge $Q$ and energy $E$ of the ions have changed due to the electron stripping and acceleration. Also the mass $M$ of some constituents of the ion beam can be different, as molecules were destroyed.

Velocity selectors or Wien filters consist of magnetic and electric fields at right angles to each other and perpendicular to the direction of the incident ions so that only ions with a specific velocity are not displaced:

$$
v^2 = \frac{2EM}{Q^2} \propto \varepsilon^2 B^2 \tag{2.6}
$$

Afterwards, the ions have to be counted. More abundant isotopes can be counted in faraday cups. These are devices that measure the charge that accumulates on them. Less abundant ions are counted with particle detectors. These have an additional advantage: They can measure the rate of the energy loss $dE/dx$ which identifies the nuclear charge $Z$:

$$
\frac{dE}{dx} \propto Z^2 \frac{1}{v^2} \tag{2.7}
$$

The identification of the nuclear charge is only possible when the abundances of the different ions are limited. When plotting the count ratio of a particle detector, a picture similar to figure 2.6 emerges. The final energy is the total energy minus the energy loss. One would expect that, when having selected the mass-14 beam, only $^{14}$C enters the particle detector so that only a $^{14}$C peak could be observed. This is not the case because ambiguities can occur.
2.1. RADIOCARBON DATING

It is for example possible that particles that are removed from the ion beam again enter the beam after small-angle scattering on residual gas particles (i.e. on gas particles that are not removed although the system is evacuated). In the particle spectrum obtained by the gas ionization detector, there are three carbon peaks (Fig. 2.6). All ions other than carbon have been removed from these spectra by means of the specific-energy-loss analysis. The difference between the carbon isotopes is too small to allow effective removal of the $^{12}\text{C}$ and $^{13}\text{C}$ interferences (Beukens, 1992). In the “E-final” (total energy minus energy loss) spectrum, the lowest energy peak is mainly due to $^{14}\text{C}$, but can include $^{12}\text{C}$ and $^{13}\text{C}$ E/Q ambiguities. Two higher peaks are due to $^{12}\text{C}$ and $^{13}\text{C}$ ambiguities. ME/Q$^2$ ambiguities can also be found. To test that these ambiguities really exist, one can introduce a pure $^{12}\text{C}$ beam into the accelerator while collecting the particle spectrum (Beukens, 1992). The reasons for these ambiguities are the following: The E/Q ambiguity is generated from particles selected by the electrostatic analysis (equation 2.4) and partially passed by the magnetic analysis through small angle scattering on the residual gas in the vacuum of the magnetic analyzers. The ME/Q$^2$ ambiguity originates from particles selected by magnetic analysis (equation 2.5) and partially passed by the electric analysis through small angle scattering on the residual gas of the vacuum. ME/Q$^2$ ambiguities are not really a background, as the ion detector is energy dispersive and $^{12}\text{C}$, $^{14}\text{C}$ and $^{13}\text{C}$ ambiguity peaks are well separated. The E/Q ambiguity is a real background as $^{13}\text{C}$ and $^{12}\text{C}$ counts are indistinguishable from $^{14}\text{C}$ counts. The main source for this is the sputter tail of the $^{12}\text{C}$ peak (Beukens, 1992).

Apart from the machine background, also the sample itself can carry a background signal, originating from the burial environment, the excavation, storage, and preparation of the sample (see pages 10, 12). In total, high-quality AMS measurements can reach a precision in pmC determination of about 0.2 to 0.3%. The accelerator background, i.e. the amount of $^{14}\text{C}$ atoms that are registered although the sample is $^{14}\text{C}$ free, can go down to a $^{14}\text{C}$ level according to 60-70,000 years. Dating is normally limited by the chemical preparation background to 50,000 years but can be better with special techniques (Tuniz et al., 2003). In total, the different background sources in different steps of the sample preparation and measurement process are, after Kirner et al. (1995):

1. Machine background: $^{14}\text{C}$ detected when the sample is $^{14}\text{C}$-free
   (a) Detector anomaly: a $^{14}\text{C}$ pulse is registered when no $^{14}\text{C}$ ion is present
   (b) Ion identification anomaly: particle of same mass/energy ratio as $^{14}\text{C}$ reaches the detector
   (c) Beam-line contamination

2. Combustion/acidification background
   (a) Materials contamination from materials in the combustion/acidification tube
   (b) Tube contamination

3. Graphitisation background
   (a) Materials contamination (e.g. catalyst)
   (b) Reaction tube contamination

4. Pseudo $^{14}\text{C}$—“dead” sample background
   (a) Sample erroneously assumed to contain no $^{14}\text{C}$
   (b) $^{14}\text{C}$ introduced into material that contains no $^{14}\text{C}$

Detector anomalies, or electronic noise, can be measured by collecting a spectrum for several days without injecting any particles into the accelerator (Beukens, 1992). Charge recombination in the detector creates a tail from the $^{12}\text{C}$ and $^{13}\text{C}$ peaks which underlies the $^{14}\text{C}$ peak. Nuclear physics techniques of spectrum analysis can be used to cope with this problem of a “tail”, but the reduced statistical precision limits the background level (Beukens, 1992).

The ion source can also introduce contamination, because only about 10% of the sample’s carbon atoms is turned into negative ions and the remaining $^{14}\text{C}$ atoms are deposited somewhere in the ion-source region (Beukens, 1992).

Kirner et al. (1995) also observed that the way of sample storing has an effect on the background value. A geologic graphite sample that was powdered and encapsulated under argon had a $^{14}\text{C}$ age...
of 69,000 BP while samples of the same material that were powdered and encapsulated in air had ages of 58-60,000 BP.

The materials contamination from graphitisation could for example been estimated by pressing pure catalyst into a target and then measuring it in the accelerator. The disadvantage of this method is that the ion beam current in this case is too small and instable for a general statement (Vandeputte et al., 1998).

In addition to $^{14}$C, also the rate of the stable carbon isotopes $^{13}$C/$^{12}$C is measured, in order to correct the $^{14}$C measurement for fractionation (for details on the $^{13}$C/$^{12}$C measurement, see section 2.2).

**Calculation and reporting of datings**

In the case of samples less than 60 years old, the nuclear bomb effect would lead to negative $^{14}$C ages (see section 2.1.3). Instead of $^{14}$C ages, the radiocarbon content is in these cases often given as percent modern carbon (pmC) or as deviation from the oxalic acid standard material ($\Delta^{14}$C). In the following, I will present how these are calculated and follow the recommendations by Stuiver and Polach (1977).

1. measurement of $^{13}$C in %e (see section 2.2) and the activity or count rate of the sample, $A_s$, and of the standard material oxalic acid, Ox-I, $A_{ox}$
2. normalize sample activity for fractionation: $A_{sn} = A_s(1 - 2(25 + ^{13}C)/1000)$
3. normalize Ox-I activity for fractionation and correct to the natural reference level: $A_{on} = 0.95A_{ox}(1 - 2(19 + ^{13}C)/1000)$. In AMS, the $^{14}$C/$^{13}$C ratio is measured, instead of $^{14}$C/$^{12}$C as in decay counting, and the factor 2 is omitted.

4. calculate the absolute international standard activity, corrected for decay between 1950 and year $y$ of actual measurement: $A_{abs} = A_{on}e^{\tau(y-1950)}$ with $\tau = 1/8267a^{-1}$

Now, the conventional radiocarbon age $t$, pmC and $\Delta^{14}$C can be calculated:

$$t = -8033\ln(A_{sn}/A_{on}).$$

if sample and Ox-I are measured in the same year.

$$\Delta^{14}C = (A_{sn}/A_{abs} - 1) + 1000\%e$$

$$pmC = 100A_{sn}/A_{on} = 100e^{-t/8033}$$

$$= 100(1 + \Delta^{14}C/1000)e^{-(1950-y)/8267}$$

8033 years is the Libby mean life of radiocarbon (used for the conventional radiocarbon age in $^{14}$C years), 8267 years is the actual mean life (see above).

### 2.1.3 Bomb $^{14}$C

$^{14}$C ages of materials in equilibrium with the atmosphere after ca. 1950 would be negative, because nuclear bomb testing in the atmosphere mainly in the late 1950s and early 1960s caused the global atmospheric $^{14}$C concentration to rise (Vries, 1958) to approximately double the pre-bomb concentration. Since then, the concentration has fallen much faster than radioactive decay alone can account for. This is due to the uptake of atmospheric radiocarbon in the biosphere and the oceans. Figure 2.8 shows an illustration of the so-called bomb spike. In surface water DIC from the oceans, the bomb spike is much less pronounced than in the atmosphere (Figure 2.9). Today, the atmospheric $^{14}$C concentration is still decreasing, but this is mostly due to the combustion
of fossil, $^{14}$C-free, fuel (Suess effect, see page 7). A release of bomb radiocarbon from the biosphere has already begun (Levin et al., 2008).

### 2.1.4 Reservoir effects

There are several possible error sources in radiocarbon dating. This section will deal with reservoir effects, but another source of too high ages should also be mentioned, the old wood effect. This occurs when e.g. a fireplace is dated by radiocarbon dating of charcoal. The true age of the wood may be much older than the age of its use in the fire. This can be the case when the wood was stored a long time before its use, e.g. as timber in a building or driftwood. But also recently felled wood can show an old wood effect, when the inner year rings are dated. These year rings can have formed centuries before the tree was felled. The preferred wood or charcoal for radiocarbon dating thus comes from small branches, in the best case with the bark preserved. Pieces of long-lived trunks are avoided when possible.

However, also short-lived samples can have too high radiocarbon ages. One of the basic assumptions in radiocarbon dating is that a sample incorporates carbon in equilibrium with the atmosphere. This can be directly, e.g. in a plant via photosynthesis, or indirectly, e.g. when an animal feeds on plants. This type of samples is also called terrestrial. When a sample obtains its carbon from another reservoir with a lower $^{14}$C level than the atmosphere, the basic assumption is no longer valid, and too high apparent ages can be obtained. The difference between the $^{14}$C age of the sample and the $^{14}$C age of a contemporaneous terrestrial sample is termed reservoir age. It is calculated by subtracting the $^{14}$C age of a terrestrial sample $^{14}$C$_T$ from the $^{14}$C age of the contemporaneous aquatic sample $^{14}$C$_A$:

$$R = ^{14}C_A - ^{14}C_T$$  \hspace{1cm} (2.8)

Where $^{14}$C$_A$ and $^{14}$C$_T$ are the $^{14}$C concentrations in the aquatic and terrestrial samples, respectively. As post-bomb terrestrial $^{14}$C ages are negative, the $^{14}$C age measured on an aquatic sample would underestimate the reservoir effect. Therefore, both the aquatic sample and a modern terrestrial sample are dated. Measurements on atmospheric $^{14}$CO$_2$ (e.g. Levin et al., 2010) provide a convenient record of the terrestrial references. The reservoir age $R$ in $^{14}$C years is calculated from the difference in $^{14}$C ratios, which are given as percent modern carbon, pmC (see section 2.1.2 and Stuiver and Polach (1977) for details on notation and reporting of radiocarbon data):

$$R = 8033 \cdot \ln \left( \frac{pmC_T}{pmC_A} \right)$$  \hspace{1cm} (2.9)

where 8033 is the conventional “Libby” mean life of $^{14}$C. Propagation of uncertainty gives

$$s(R) = 8033 \cdot \sqrt{\left( \frac{\Delta pmC_A}{pmC_A} \right)^2 + \left( \frac{\Delta pmC_T}{pmC_T} \right)^2}.$$  \hspace{1cm} (2.10)

I assume that the pmC of atmospheric CO$_2$ was measured with greater precision than the pmC of the aquatic samples, so the uncertainty of the atmospheric measurement pmC$_T$ is negligible and the above equation simplifies to

$$s(R) = 8033 \cdot \frac{\Delta pmC_A}{pmC_A}.$$  \hspace{1cm} (2.11)

As the slope of the bomb pulse is very steep (Figure 2.8), small changes in the true age of source carbon can lead to high changes in $^{14}$C ages. For the $^{14}$C content of the contemporaneous atmosphere at the time of sample formation, pmC$_T$, measurements from the Black Forest station Schauinsland are used (Levin et al., 2010 and pers. comm. 2012). In spite of the high altitude, they are assumed to be a better estimate than the available data from a low-altitude station, Heidelberg, in the heavily polluted Rhine-Neckar area, which is affected both by additional $^{14}$C from a nearby nuclear power plant and $^{14}$C-free CO$_2$ from industry, heating and transport (Levin et al., 2008). As the reservoir effect is the difference in $^{14}$C age between an aquatic sample and the $^{14}$C age of a contemporaneous terrestrial sample, water DIC $^{14}$C-concentrations measured in this study will be compared with those of the atmosphere in the month of sampling, and aquatic plant $^{14}$C-concentrations with the average atmospheric concentrations of the entire growing season during which the plant grew (April-September, or April-July/August in case of sampling in summer).

Figure 2.10 shows the radiocarbon content of a terrestrial sample (solid line) and of a sample from a reservoir with only 80% of the atmospheric $^{14}$C level, evolving over time according to the decay law (Figure 2.1). The measurement of a certain $^{14}$C concentration (in this case, 0.5 of the atmospheric concentration) of the non-terrestrial sample leads to a too high age (a), if the initially lower $^{14}$C concentration is not considered. If one had known the original $^{14}$C concentration of the reservoir, the right age (b) would have been found. There are two important reservoir effects, both in aquatic systems: the marine and the freshwater reservoir effect.

**The marine reservoir effect**

The atmosphere and the biosphere are regarded as forming the same radiocarbon reservoir, but they only
contain 7% of the global carbon, 5% in the biosphere and 2% in the atmosphere. The largest carbon reservoir on Earth are the oceans, containing 93% of the global carbon. The ocean can be divided into two parts, the surface water and the deep water. Both are well mixed individually, and apart from regions of upwelling or deep-water formation, there is little exchange between them (cf. Figure 2.11). There is 100 times as much deep water as surface water. The carbon in the deep water is isolated from exchange with the atmosphere, before it wells up again and is mixed with surface water. During the long residence time, the $^{14}$C in the deep water decays without being replaced by new $^{14}$C from the atmosphere. The activity of deep water is thus considerably lower than the activity of surface water (Olsson, 1976). In the surface water, the mixed layer of the ocean, exchange with atmospheric CO$_2$ and old carbon from the deep ocean combine to a reservoir effect of about 400 years (Stuiver et al., 1986). For the calibration of marine samples, a calibration curve (Figure 2.12) is modelled from the terrestrial curve, e.g. IntCal09 (Figure 2.2), by applying a diffusive box model of the global carbon cycle (Stuiver and Braziunas, 1993; Hughen et al., 2004; Reimer et al., 2009). Often, it cannot be assumed that a marine sample was part of the uniform surface ocean reservoir. Regional offsets, termed $\Delta R(t)$, of the reservoir age can be caused by influx of carbonate-rich freshwater (see below and e.g. Heier-Nielsen et al., 1995) or by upwelling of deep water, and can result in offsets between a few hundred and up to thousand years (e.g. Ingram and Southon, 1996; Mangerud and Gulliksen, 1975). The Danish fjords are an example of a mixing of two carbon reservoirs, marine and freshwater. Danish Baltic Sea areas like the Skagerrak-Kattegat and the Belts show the same reservoir age as the North Sea and North Atlantic: about 400 years. In contrast to that, the Danish fjords have higher and more scattered ages between 400 and 900 years and are thus not part of the uniform marine reservoir. The variability in the reservoir ages of the fjords is explained with different concentrations of old dissolved carbonate (Heier-Nielsen et al., 1995).

Similar to the reservoir age (equation 2.8), the local
2.1. RADIOCARBON DATING

Figure 2.9: The bomb pulse in atmospheric CO₂ and in the dissolved inorganic carbon in near-surface seawater. The annual total atmospheric testing of thermonuclear bombs is given in megatons (Clark and Fritz, 1997).

\[
\Delta R = ^{14}C_M(t) - ^{14}C_{\text{MAR}}(t). \tag{2.12}
\]

Via photosynthesis, plants incorporate the carbon from the \(^{14}\text{C}\)-depleted DIC. From the phytoplankton via the zooplankton and fish, this “old” carbon finally also ends in food for animals living on land. One example are recent polar bears from Svalbard and East Greenland which had \(^{14}\text{C}\) ages of 480±70 and 495±45 years, respectively (Olsson, 1976). The same effect can of course be found in humans (e.g. Olsson, 1976; Arneborg et al., 1999; Lanting and van der Plicht, 1995/1996). In this case, \(\delta^{13}\text{C}\) measurements can be used for calculating the percentage of aquatic food in an individual’s diet (see section 2.2.1). The \(^{14}\text{C}\) age of the humans can then be corrected by the correspondent fraction of the marine reservoir age (Arneborg et al., 1999).

The freshwater reservoir effect

Dissolved inorganic carbon (DIC) in the water is the basis for photosynthesis. A common source of “old”, i.e. \(^{14}\text{C}\)-depleted, carbon is dissolved carbonate from \(^{14}\text{C}\)-free carbonate minerals, but also from the de-
composition of other rocks such as volcanic glasses (Sveinbjörnsdóttir et al., 1995). Other old carbon sources include CO$_2$ from decaying organic matter in the catchment or organic matter that is washed into the rivers and mineralized there. Organic material can both be contemporaneous terrestrial vegetation, but also old material from a peat bog (Goh, 1991). Also a long residence time of water in a lake or aquifer can lead to high $^{14}$C-ages (Håkansson, 1976; Culleton, 2006).

As carbonate-rich water is called hard water, the freshwater reservoir effect caused by dissolved carbonate minerals is often termed hardwater effect. Details on the mechanisms leading to a hardwater reservoir effect can be found in Clark and Fritz (1997) and Fontes and Garnier (1979). The hardwater effect is expected to be greater in running water like rivers than in stagnant water like lakes. If there is not a noticeable meltwater component, river water consists largely of groundwater which on its way through the underground can dissolve substantial amounts of carbonates, if present (Lanting and van der Plicht, 1995/1996). In the following discussion, I will prefer the term freshwater reservoir effect over hardwater effect, as it often cannot be said with certainty whether high apparent ages in a freshwater system solely are caused by dissolved old carbonates, or whether other sources of old carbon should be considered as well. Although I studied the reservoir age in rivers (chapter 6), lakes are often used as examples in the following introduction. This is mainly due to the fact that the primary studies focused more on lakes than on rivers. However, most processes found in lakes are also important in rivers. As one of the rivers I studied flows through a lake, some of the information presented on lakes will be useful for the discussion of my results.

The hardwater effect was predicted by J. Iversen in a private communication to E. S. Deevey, October 5, 1949 (Oana and Deevey, 1960). The effect was considered by Godwin (1951) when discussing radiocarbon dates from the British Isles, and measured for the first time in 1954 (Deevey et al., 1954). A freshwater reservoir effect has also been found in human bones due to freshwater fish consumption (Lanting and van der Plicht, 1995/1996; Cook et al., 2001; Smits and van der Plicht, 2009; Olsen and Heinemeier, 2009; Olsen et al., 2010a; Shishlina et al., 2007) or in food crusts on pottery when freshwater resources had been
prepared in the vessels (Boudin et al., 2009b; Fischer and Heinemeier, 2003; Philippson, 2010; Philippson et al., 2010). Freshwater reservoir ages can be between zero and several thousand years, so a calibration or correction is more complicated than with marine samples from the well-mixed surface ocean (see above). For correcting the radiocarbon dating of human bones, the full reservoir effect is calculated from associated aquatic and terrestrial samples, e.g. seeds and fish-bones (Shishlina et al., 2007). The proportion of aquatic diet in the humans is estimated by a δ13N measurement (see section 2.2.2), and the dating is corrected by the corresponding fraction of the full reservoir effect (e.g. Cook et al., 2001; Shishlina et al., 2007; Bonsall et al., 2004). Freshwater reservoir effects can show a lot of variation within a lake or river (Srdoč et al., 1980; Olsson and Kaup, 2001; Philippson et al., 2010), even when only regarding submerged plants (Olsson and Kaup, 2001), or a single species of fish from one lake (Keaveney and Reimer, 2012). This will be discussed in detail in section 2.3, together with δ13C values in freshwater systems.

2.2 Stable isotope measurements

In this study, the abundances of the stable carbon, nitrogen and oxygen isotopes 13C, 15N and 18O are measured. All these elements must be isolated and converted to a gas that is stable and unreactive at room temperature (Boutton, 1991). The gases used here are CO₂ and N₂. Organic samples are combusted in an elemental analyser yielding CO₂ and N₂. As oxygen is added during the combustion, the CO₂ does not retain the original 18O/16O signal of the sample. Inorganic samples (shell carbonate and water DIC) are acidified to yield CO₂ on which 13C/12C and 18O/16O can be measured.

The range of possible isotope ratios in nature is quite narrow. The most enriched materials of biological interest differ from the least enriched by only 10% (Boutton, 1991). They are therefore quoted as δ deviations in ‰ from a reference material. With e.g. the 13C/12C isotope ratios of the sample and standard, 13R_{sam} and 13R_{std}, the δ notation is

\[ \delta^{13}C = \frac{13R_{sam} - 13R_{std}}{13R_{std}} \times 1000 \text{‰}. \]  

The same notation is used for δ15N and δ18O.

In the 1970s, the potential of stable isotope analysis for diet reconstruction was discovered, after the different fractionation between C₄ (in this case maize) and C₃ plants had been observed (Tykot, 2003). There are also differences in the 13C or 15N values in bones of populations that lived mainly on terrestrial or marine food, respectively. Measurements of stable isotopes make it thus possible to reconstruct past diets. The most commonly used stable isotopes for this purpose are 13C and 15N, which I also used to analyse food crusts on pottery and sediment samples. δ13C and 18O of shell carbonate or δ18O of water can be used in studies of palaeoenvironment, -climate and -salinity.

2.2.1 δ13C

For 13C, δ13C values were calculated with respect to the standard material Pee Dee Belemnite, a Cretaceous belemnite from the Pee Dee formation in the south-eastern USA. It was formed during the Cretaceous period from the fossils of the marine cephalopods Belemnoidea, in this case Belemnitella americana (Tuniz et al., 2003). Its absolute 13C/12C ratio is 0.0112372 (Craig, 1957). As the original standard material is exhausted, newer measurements are reported with respect to the scale “Vienna Pee Dee Belemnite” (VPDB), which was calibrated against the standard material NBS 19, another carbonate.

For all 14C dated samples, δ13C measurements have been performed in order to correct for fractionation. Apart from that, δ13C measurements can give additional information about the samples. Fractionation (see page 5) causes different materials or environments to have different δ13C ratios. The following account focuses on fractionation

1. at the water-atmosphere boundary
2. between the atmosphere and terrestrial plants (during different types of photosynthesis) and during uptake by animals and humans
3. after deposition in the soil, i.e. during diagenesis

δ13C values in freshwater systems will be discussed in detail, together with the freshwater reservoir effect, in section 2.3.

δ13C in atmosphere and ocean δ13C can be used to differentiate between marine and terrestrial food sources as the food chains in these environments begin with different 13C ratios in the CO₂.

CO₂ is exchanged between the atmosphere and the oceans by diffusion. The δ13C value of dissolved inorganic carbon (DIC) is salinity-dependent. The reason is that fractionation occurs in the hydration stage, not when CO₂ passes the air-water interface (Degens, 1969). The equilibrium fractionation for the process

\[ 13\text{CO}_2 + \text{H}^{12}\text{CO}_3 \rightleftharpoons^{12}\text{CO}_2 + \text{H}^{13}\text{CO}_3 \]  

(2.14)
is 9.2% at 0°C and 6.8% at 30°C (the CO₂ is \(^{13}\)C-depleted).

In sea water with a pH of 8.5, more than 99% of the DIC occur in the form of HCO₃⁻. Sea water DIC is thus isotopically heavier than atmospheric CO₂ (Degens, 1969; Craig, 1954). Air CO₂ had δ\(^{13}\)C = -6.4% prior to the combustion of fossil fuel. Now, the value is lower (Tans et al., 1979). Marine DIC has δ\(^{13}\)C \(\approx 0\)%\(\text{e}\) (the standard PDB is a marine carbonate).

During photosynthesis by water plants, the same fractionation takes place as in terrestrial plants (see below). The isotopic difference between land and sea at the basis of the food chain is thus transferred to higher trophic levels and δ\(^{13}\)C can be used to distinguish materials of marine from those of terrestrial origin. δ\(^{13}\)C values for marine animals were found to be in average 5.5% less negative than for terrestrial animals (Schoeninger and DeNiro, 1984). Humans who live mainly on marine food, have δ\(^{13}\)C values in their bone collagen of -13±1%\(\text{e}\) (Lanting and van der Plicht, 1995/1996; Chisholm et al., 1982). A purely terrestrial diet would lead to δ\(^{13}\)C values of -20%\(\text{e}\) (Chisholm et al., 1982).

\(\delta^{13}\text{C and photosynthesis}\) If not indicated otherwise, information about δ\(^{13}\)C and photosynthesis was extracted from Clark and Fritz (1997). Fractionation can happen at different stages in photosynthesis:

1. CO₂ diffusion into the leaf stomata
2. dissolution in the cell sap
3. carboxylation (carbon fixation) in the chloroplast of the leaf, where CO₂ is converted to carbohydrate (\(C_n(H_2O)_m\)).

Carboxylation is the addition of CO₂ to an organic molecule that acts as a CO₂ acceptor (Craig, 1954). The first stage in photosynthesis lead to fractionation because the velocity of gas molecules is mass-dependent:

\[
\frac{v(\text{^{12}CO}_2)}{v(\text{^{13}CO}_2)} = \sqrt{\frac{45}{44}} = 1.011 \tag{2.15}
\]

where \(v\) is the velocity of the gas molecule. In this example, the oxygen in the \(^{12}\)CO₂ is the lightest isotope, \(^{16}\)O. Collisions of \(^{12}\)CO₂ with a photosynthesizing leaf are according to this equation 1.1% more frequent than of \(^{13}\)CO₂ (Degens, 1969; Craig, 1954).

Three photosynthetic pathways occur in plants and result in different isotope ratios. The evolutionarily oldest photosynthesis pathway, called Calvin or \(\text{C}_4\) cycle, is particularly suited to wet and mesophytic, i.e. moderately humid, environments (Brownman, 1981). It is called \(\text{C}_4\) cycle because the first product of photosynthetic CO₂ fixation is a 3-carbon-compound (Hibberd and Quick, 2002). It operates in about 85% of plant species, including most trees and agricultural plants. Plants growing higher than 40 degrees of latitude use exclusively the \(\text{C}_3\) cycle. The \(\text{C}_3\) cycle developed when the earth’s atmosphere contained more CO₂ than today. \(\text{C}_3\) plants fix CO₂ with the Rubisco enzyme, which also catalyses CO₂ respiration through reaction with oxygen. In the present day’s atmosphere, CO₂ respiration is an inefficiency, only remaining as an artefact from development in an atmosphere with high CO₂. Diffusion and dissolution of CO₂ lead to a net enrichment in \(\text{C}_3\), whereas carbon fixation leads to a 29% depletion. The δ\(^{13}\)C values for \(\text{C}_3\) plants end up as -24 to -30%\(\text{e}\). \(\text{C}_3\) plants are preferred by herbivores because they are more digestible. Overgrazing causes therefore plants with other photosynthesis pathways to become dominant.

The \(\text{C}_4\) pathway, also called Hatch- Slack cycle after its discoverers, evolved as atmospheric CO₂ concentrations began to decrease in the early Tertiary. Under low CO₂:\text{O}_2 conditions and at higher temperatures, increased respiration in \(\text{C}_3\) plants interferes with their ability to fix CO₂. In this environment, the \(\text{C}_4\) cycle is thus more efficient. The name \(\text{C}_4\) comes from the 4-carbon-compound which is the first product of photosynthetic CO₂ fixation. \(\text{C}_4\) is a partly closed system and not able to discriminate as completely as \(\text{C}_3\) against the more energy-expensive heavier isotopes. \(\text{C}_4\) plants incorporate so a bigger ratio of \(^{13}\)C and \(^{14}\)C than \(\text{C}_3\) and appear too young when they are compared to contemporaneous wood samples without δ\(^{13}\)C correction. They have δ\(^{13}\)C values of -12.5%\(\text{e}\) in average, ranging from about -10%\(\text{e}\) to about -16%\(\text{e}\). 5% of the known plant species are \(\text{C}_4\) plants. They dominate in hot open ecosystems such as tropical and temperate grasslands. Some important agricultural plants like sugar cane, corn and sorghum are \(\text{C}_4\) plants. Very few edible \(\text{C}_4\) plants, such as Purslane (\(\text{Portulaca oleracea}\)), are native to Northern Europe. The first agricultural \(\text{C}_4\) plant that came to Northwestern Germany and Denmark was millet, introduced in the Bronze Age. It never gained a large importance, but could have been used as a reserve in case of an ongoing failure of other cereal crops. Millet grows very fast and needs much less time from sowing to harvesting than other cereals (Jensen, 2002).

Some \(\text{C}_3\) plants might have the potential to develop \(\text{C}_4\) photosynthesis, as recently was found out for tobacco. \(\text{C}_4\) photosynthesis has evolved independently many times (Hibberd and Quick, 2002).

Another photosynthesis pathway developed in arid regions: The Crassulacean acid metabolism (CAM) cycle which is used by about 10% of plants. This
pathway sometimes operates as an open and sometimes as a closed system, determined by environmental conditions. Therefore, it is well adapted to water-stressed environments. CAM plants have the ability to switch from C3 photosynthesis during the day to the C4 pathway for fixing CO2 during the night. Many CAM plants can shift to a C3-like mode of photosynthesis and grow faster when enough water is available (Browman, 1981). The δ13C values of CAM plants span the whole range of C3 and C4 plants, usually having intermediate values.

Further fractionation takes place along the steps of the food chain, from plant food to animal bone collagen about 5%, and generally only less than one per mil for the subsequent steps, e.g. from herbivore bone collagen to carnivore bone collagen (Schoeninger and DeNiro, 1984; Katzenberg et al., 2000; Lanting and van der Plicht, 1998, see also section 2.4.2). Even in different materials from the same organism, different δ13C values can be found. An African browsing ungulate, for example, had a δ13C value of -21.2‰ for the bone collagen, but -28.9‰ in the fat (Browman, 1981).

Proteins in tissues of the consumer are mainly derived from proteins in the food. Carboneate in bone apatite is derived from blood CO2 and ultimately from all energy supplying components in the diet, including excess protein. The carbonate fraction therefore reflects the mean isotopic composition of the whole diet (Lanting and van der Plicht, 1995/1996). Experiments with rats show that δ13C values in bone collagen not only depend on the δ13C values of the protein in the food but also on the amount of protein and on the difference in δ13C values of protein and non-protein fractions. The δ13C values in bone collagen could thus overestimate the amount of protein in the food, especially when this contains limited amounts of protein. The explanation is that proteins are used in the first place to produce tissues like collagen, and are only used as energy suppliers in case of excess. Although δ13C values of bone collagen might overestimate the amount of protein in the diet, they give valuable information by indicating the protein source of a population.

δ13C in soil Some diagenetic processes can enrich the organic matter in soils in 13C, whereas diffusion of CO2 in soil leads to δ13C enrichment. The main mechanisms in the early diagenetic fractionation of carbon isotopes are linked to the removal of 13C-rich compounds such as proteins or carbohydrates, or the decarboxylation of molecules, as the carboxyl carbon is 13C enriched. The remaining material in the sediment becomes thus isotopically lighter while 13C-enriched CO2 is released (Degens, 1969). The decay of organic material in the soil does not lead to further fractionation. Aerobic bacteria convert much of the organic material back to CO2, and this CO2 has much the same δ13C concentration as the vegetation itself. The CO2 concentration of soils is 10 to 100 times as high as that of the atmosphere, and it is diffusion of CO2 along this steep concentration gradient that results in a 13C enrichment of ≥4‰ of the soils. δ13C in soils hosting C3 plants is about -23‰, whereas it is -9‰ in a C4 landscape (Clark and Fritz, 1997).

2.2.2 δ15N

The 15N/14N ratio is, just like 13C, expressed in the delta notation. The standard material for 15N is atmospheric air (AIR). In this case, we benefit from a different fractionation effect. There is an enrichment of 15N with each step between trophic levels (Ambrose, 2001). This means that there is 15N enrichment from plants to herbivores to carnivores. Marine and freshwater zooplankton, for example, have δ15N values that are on average 3‰ more positive than associated phytoplankton (Schoeninger and DeNiro, 1984, and references therein). In aquatic systems, food chains are generally longer than in terrestrial systems, so that more 15N enrichment steps can take place. The terrestrial system in most ecosystems has only three levels: plants, herbivores and carnivores. Enrichment between two steps in a food chain is normally about 3‰, but there are big differences between species (Ambrose, 2001). Furthermore, trophic levels can overlap to a large extent (Schoeninger and DeNiro, 1984). Humans who live on a 100% aquatic diet have δ15N values of 16-18‰ in their bone collagen (Schoeninger et al., 1983; Cook et al., 2001). There is a large variation, though, depending on what aquatic food was consumed (small fish, for example, result in lower, seals in higher δ15N values).

Fractionation might furthermore occur during denitrification, nitrogen fixation and mineralisation of organic nitrogen (Blackburn and Knowles, 1993). δ15N values in the organic matter of aquatic systems may depend on primary organic productivity or δ15N values of dissolved nitrogen from the catchment (see chapter 7 for details).

2.2.3 δ18O

Two common materials for δ18O measurements are water and shell carbonate. One standard for δ18O is the same as for δ13C, VPDB. This is commonly used when measuring shell carbonate. For water, another
\[ \delta^{18}O_{SMOW} = 1.03086 \cdot \delta^{18}O_{PDB} + 30.86 \]  
and 
\[ \delta^{18}O_{PDB} = \frac{\delta^{18}O_{SMOW} - 30.86}{1.03086} \]

\( \delta^{18}O \) values in precipitation are depleted relative to the ocean because of fractionation processes during evaporation (Araguas-Araguas et al., 2000; Dansgaard, 1964; Emeis et al., 2003). Precipitation collected in Cuxhaven, north-western Germany, in 1978-2005, for example, has values ranging from -15.61 to -1.26\% VSMOW (IAEA/WMO, 2006). The average for the whole period from January 1978 to December 2005 is \( \delta^{18}O = (-6.98 \pm 1.88)\% \) VSMOW, which is quite close to the “standard value” for meteoric water of \( \delta^{18}O = -7.5\% \) SMOW that was reported for the British Isles (Andrews et al., 1993). During winter, when a mixture of snow and rain was collected, the range in the precipitation collected in Cuxhaven was shifted towards more negative values (-15.61 to -2.23\% VSMOW) than during the rest of the year, when only rain was collected (-11.41 to -1.26\% VSMOW). However, there is a great overlap of \( \delta^{18}O \) values.

River water is a mixture of meteoric water and groundwater, the latter of course being recharged by meteoric water as well. The \( \delta^{18}O \) value of river water represents thus an average of the precipitation that fell within the watershed (Andrews et al., 1993), while single storm events still are discernible (Criss, 1999). The GNIR database (Global Network of Isotopes in Rivers, http://www-naweb.iaea.org/napc/ih/IHS_resources_gnir.html) provides \( \delta^{18}O \) records of river water. Values in northern German rivers (Elbe, Ems, Fulda, Werra and Weser) in 2007-2008 vary between ca. -8.5 and -6.5\% VSMOW, occasionally up to -4\% (Koeniger et al., 2009, and unpublished data from M. Elnser and W. Stichler (Heilmoltz-Forschungszentrum München)). At the mouth of the Schelde, however, values greater than -4\% VSMOW are quite common (data obtained from RUG Groningen, CIO), probably due to evaporation (pers. comm. Stefan Terzer 2012).

Shells reflect the \( \delta^{18}O \) value of the water in which they grew. The fractionation between water and shell is temperature- and salinity-dependent. Shell \( \delta^{18}O \) values reflect thus global climate, local water temperature and salinity. \( \delta^{18}O \) of marine shells can thus be used for palaeoclimate reconstruction - during glaciations, isotopically light water was frozen in ice caps, and the sea water was correspondingly enriched in \( ^{18}O \). However, low water temperatures lead to high \( \delta^{18}O \) values of shells (Mook, 1971).

Isotopic signals from shells and bulk sediments have been commonly used for quantitative salinity reconstruction (Punning et al., 1988; Winn et al., 1988, 1998), often in combination with \( \delta^{13}C \). Winn et al. (1988) measured \( \delta^{13}C \) and \( \delta^{18}O \) of the benthic foraminifera Ammonia beccarii and \( ^{14}C \) and \( \delta^{13}C \) of the organic fraction of the sediment. They found a fast sea level rise in 8000-7000 BP where the salinity increased with 13-15\% and a short episode around 6000 BP where salinity decreased by 9\%. Burman and Schmitz (2005) found from \( \delta^{18}O \) measurements on periwinkle shells from the Ertebølle kitchen midden that the salinity of the Limfjord was higher in the EBK than today. (Mook, 1971) found a positive correlation between \( \delta^{13}C \) and \( \delta^{18}O \) values of shells from estuarine waters in the Netherlands, and used this information for palaeosalinity reconstruction.

In this study, \( \delta^{18}O \) measurements will be performed on shells from a sediment core. Furthermore, \( \delta^{18}O \) will be measured on water DIC, not the water itself, as \( \delta^{18}O \) measurements on water DIC are readily available during \( \delta^{13}C \) measurements. \( ^{18}O \) in the different dissolved carbonate phases (DIC) exchanges rapidly with the water, so that DIC \( \delta^{18}O \) reflects water \( ^{18}O \) (Clark and Fritz, 1997). The DIC is extracted as CO\(_2\) gas, and the fractionation factor between CO\(_2\) (g) and water is \( 10^3 \ln \alpha = 40.1 \) at 25\°C (Bottinga, 1968, for details on calculations of isotopic fractionation, see Clark and Fritz, 1997.). It should be kept in mind, however, that the \( \delta^{18}O \) measurements of DIC and those on water are not completely equivalent, so the \( \delta^{18}O \) measurements on DIC cannot be used to draw accurate hydrological conclusions.

### 2.3 \( ^{14}C \) and \( ^{13}C \) in freshwater

The conditions for plants in freshwater systems are different from those in atmospheric air. There are different ways to cope with these challenges. Different plant species have found different adaptations. I will address two species in detail, the yellow and the white water lily, Nuphar lutea and Nymphaea alba, as they provide some interesting problems for radiocarbon dating. Aquatic plants assimilate carbon from dissolved inorganic carbon, DIC. In the following, I will explain the properties, origins and possible radiocarbon ages and \( ^{13}C \) values of DIC, before I explain the characteristics of aquatic plants and their radiocarbon ages.
DIC  An excellent introduction into, among other isotopes, the stable and radioactive carbon isotopes in water systems can be found in Clark and Fritz (1997). Dissolved inorganic carbon, DIC, comprises four species:

- Carbon dioxide CO$_2$
- Carboxylic acid H$_2$CO$_3$
- Bicarbonate anion or hydrogen carbonate HCO$_3^-$
- Carbonate anion CO$_3^{2-}$

Carbonic acid is the predominant acid in natural waters and most responsible for rock weathering (Lambrini, 1997). The first two species, CO$_2$ and carbonic acid, are often summed up as CO$_2$ because the carbonic acid only exists in aqueous solution and dissociates immediately. In the following discussion, I will therefore exclude the carbonic acid, and only discuss the remaining three DIC species. The bicarbonate anion HCO$_3^-$ is an amphoteric substance, it can both donate and accept protons. Bicarbonate is the conjugate base of carbonic acid H$_2$CO$_3$ and the conjugate acid of the carbonate ion CO$_3^{2-}$:

$$\text{CO}_3^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_2\text{O} + \text{OH}^-$$
$$\leftrightarrow \text{H}_2\text{CO}_3 + 2\text{OH}^-$$
$$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$$
$$\leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+$$

(2.18)

The concentration of HCO$_3^-$ and CO$_3^{2-}$ together is called carbonate alkalinity.

Alkalinity in general denotes the concentration of dissolved species which act as proton acceptors and buffer pH, i.e. consume acidity. The inorganic carbon is mainly controlled by acid-base reactions. The distribution of the DIC species, CO$_2$, HCO$_3^-$ and CO$_3^{2-}$, is largely a function of pH (St-Jean, 2003). The three DIC species are related in the following pH controlled chemical equilibrium:

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$$
$$\leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}$$

(2.19)

At pH values typical of natural waters, bicarbonate is the dominating DIC species (Broecker and Walton, 1959).

The DIC enters the water system in the following way: Precipitation percolates through soil and bedrock. In the soil, root respiration and the decay of organic material release CO$_2$. This CO$_2$ can have a recent $^{14}$C activity, or be depleted in the case of old organic matter, and $^{13}$C$_{atm} = -25\%$. In contact with rain water percolating through the soil, a small amount of this CO$_2$ is dissolved in the rain water and forms carbonic acid (H$_2$CO$_3$). The amount of CO$_2$ that can dissolve depends on temperature, initial water pH and the partial pressure of CO$_2$. The higher the CO$_2$ concentration in the soil atmosphere, the lower the initial pH. Although rainwater contains some CO$_2$ from the atmosphere, the groundwater's radiocarbon signal is dominated by the carbon from the soil zone, as the partial CO$_2$ pressure in soil is much larger than in the atmosphere. In the deeper subsoil this dissolved CO$_2$, i.e. carbonic acid, dissolves carbonates, and the low pH of the water is buffered by the mineral weathering, e.g.

$$\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$$
$$\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^-$$

(2.20)

$$\vdash \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$

The carbon of inorganic origin is thus a mixture of active carbon from soil gas CO$_2$ and old carbon from carbonate in the subsurface. 1/2 mole of atmospheric CO$_2$ is added to the system for each equivalent of Ca and Mg dissolved so that 1/2 of the total CO$_2$ is $^{14}$C-free while the other half has atmospheric concentration. Fossil carbonate from the subsoil has no $^{14}$C activity and $^{13}$C$_{atm} + 1\%$. When finally equilibrium is reached, CO$_2$ in groundwater has only half the “recent” $^{14}$C activity and its $^{13}$C is ca. -12%. Figure 2.13 from Clark and Fritz (1997) summarizes the processes in the soil. The concentration of the alkaline earth metal ions, predominantly calcium (Ca) and magnesium (Mg), is also termed “water hardness”. Carbonate dissolution is often automatically considered as an index of $^{14}$C dilution and reported as the “hardwater effect” (see section 2.1.4). However, single examples show exceptions from this general rule (Fontes, 1992). A measurement of the water hardness indicates therefore the possibility of a hardwater effect, but is not sufficient to quantify the dilution of $^{14}$C content in the water.

While carbonate dissolution (equation 2.20) leads to “old” DIC in the water, the weathering of other types of rock only adds atmospheric/root zone CO$_2$ to the water. In the following example, the plagioclase feldspar anorthite CaAl$_2$Si$_2$O$_8$ (a silicate mineral) is dissolved:

$$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$$
$$2\text{OH}^- + 2\text{CO}_2 \rightarrow 2\text{HCO}_3^-$$

(2.21)

$$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{H}_2\text{O} + 2\text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$$

Each equivalent of Ca, Mg, Na, and K ions dissolved from silicate minerals is accompanied by the addition of 1 mole of atmospheric/root zone CO$_2$. No HCO$_3^-$ from minerals is added in this case (Broecker
and Walton, 1959). The only change to the carbonate system is the increase in pH that is associated with silicate dissolution. This increase in pH shifts the distribution of DIC species towards a dominance of HCO$_3^-$ in the system, i.e., if further exchange is possible, additional CO$_2$ will be dissolved from the soil zone. In any case, the DIC from silicate weathering is derived solely from soil CO$_2$.

The $^{14}$C age of surface water DIC approaches the atmospheric $^{14}$C level by CO$_2$ exchange over the water-air boundary. CO$_2$ exchange rates for rivers can be as high as 100 moles/m$^2$, whereas CO$_2$ exchange rates in inland lakes are about 5 moles/m$^2$ (Broecker and Walton, 1959).

When radiocarbon dating water samples, one can correct for the contribution of dissolved carbonates to the radiocarbon age. To correct the measured $^{14}$C concentration, the $\delta^{13}$C value of the water is measured. If assuming that fossil carbonate has a $\delta^{13}$C value of about 0‰ and CO$_2$ from the root zone has -25‰, the corrected $^{14}$C activity of the water is

$$A_d = A_m - \frac{25}{\delta^{13}C_m} \quad (2.22)$$

with the measured activity $A_m$. The radiocarbon age is now calculated with the corrected activity, $A_d$ (Boaretto et al., 1998). The $^{14}$C age measurement can also be corrected by estimating the initial $^{14}$C activity $A_{in}$ that originates from the dilution of the atmospheric activity $A_{atm}$ with fossil carbonate:

$$A_{in} = A_{atm} \frac{\delta^{13}C_m}{-25} \quad (2.23)$$

However, this correction assumes that dissolved carbonate and recent CO$_2$ from the root zone are the only DIC sources. Atmospheric exchange and mineralisation of old organic matter are not considered.

**DOC** In addition to the inorganic carbon, organic carbon is also present in freshwater systems. The dif-
ferent organic carbon species are not defined chemically, but just according to particle size: The particle size of dissolved organic carbon, DOC, is smaller than 0.45 μm. Organic carbon with particle sizes bigger than 0.45 μm is called particulate organic carbon. Organic carbon can enter the food chain via two pathways: direct uptake by filter feeders such as some molluscs, or mineralisation to DIC. The DOC originates from chemical and physical changes in soil organic matter (SOM) that becomes soluble (St-Jean, 2003) and is stored in the soil waters. The concentration of DOC in soil moisture can reach a maximum of 10 to 100mgC/L in the root zone. This concentration drops off towards the water table. Groundwaters often have less than 1 to 2 mgC/L DOC (Clark and Fritz, 1997). An example is a study of the lake Schweriner See in north-eastern Germany. Two parallel food chains could be identified by radiocarbon dating of DIC, POC and several plants and animals. One food chain proceeds from DIC through phytoplankton, zebra mussels, and fish, the other from POC through eels specializing on zooplankton (Ricardo Fernandes, under prep). Different methods can be used for extracting the DOC. Gandhi et al. (2004) concentrated 150 to 200 mL stream water, containing about 20 μmol C by rotary evaporation to about 1 mL±0.5 mL and added 85% phosphoric acid until pH 2 to remove DIC. 300 μL of the sample were step-wise transferred to silver capsules and dried at 70°C. Alternatively, in an older method, 1-2 mL of concentrated sample were acidified, transferred to a quartz tube and freeze-dried, before CuO and Cu were added and the tube sealed and combusted (Gandhi et al., 2004). As these methods only were used for 13C analyses, much larger sample sizes would be required if we used the same methods for DOC extraction for radiocarbon dating (about 5 times as much).

Seasonal variability and secular changes When measuring the reservoir age of a water system, it has to be taken into account that the 14C content of the water can be subject to seasonal or secular changes. The dating of one water sample only, taken at a special time, can therefore be not more than an estimate of the reservoir effect (Geyh et al., 1998). Lakes are subject for the biggest changes because there is no continuous flow of water. However, it will be shown later that rivers exhibit considerable reservoir age variations as well (chapter 6).

Temporal changes in the hardwater effect are due to water temperature and biological activity. Bicarbonate for example is probably periodically concentrated in lakes by evaporation (Culleton, 2006). In late summer, lakes are often thermally stratified with warm water in the upper layers and colder water in the bottom of the lake. Towards winter, the upper layers cool down due to the sinking air temperatures until their density exceeds that of the layers below, which are still a little bit warmer. Cool water from the upper layers sinks thus down and the lake water gets mixed by this process. When water with different bicarbonate concentrations gets mixed, an excess CO2 concentration builds up which increases during winter due to the decomposition of organic matter. In spring, the upper water layers warm up and biological activity begins. Inorganic carbon precipitates due to the biological removal of CO2 and to a lesser extend due to degassing in the warm summer. This takes place in the upper layers of the lake where there is enough light for intensive biological activity. Carbonate that was precipitated through this process reaches the lake ground only when the water in the bottom layers is supersaturated with CO2. Sedimentation takes thus mainly place at the end of the warmer season. Total dissolved inorganic carbon (TDIC) and precipitated carbonate should be in equilibrium, but as there can be more exchange with atmospheric CO2 the more carbon in the original DIC reservoir is biologically removed, the 14C value increases with decreasing carbonate sedimentation rate (Geyh et al., 1998).

Sedimentation can decrease the reservoir age of a lake. The extent of the hardwater effect depends on the surface-to-volume-ratio of a lake. It is thus basically dependent on the water depth, as the surface of a lake with outflow only changes minimally when the water depth decreases because of sedimentation (Geyh et al., 1998). The reason for the dependence on the surface-to-volume-ratio is that exchange with the atmosphere only takes place at the water surface while the dissolved inorganic carbon reservoir is proportional to the entire volume. When thus the water depth decreases because of a rising of the lake ground due to sedimentation, the water volume gets smaller while the lake surface still is the same. There is thus the same exchange with CO2 from the atmosphere while the total amount of dissolved inorganic carbon decreases with the decreasing amount of water in the lake. Sedimentation in a lake is thus a reason for secular changes in the reservoir age. Sedimentation could also cut off the supply of groundwater to the lake so that the amount of dissolved inorganic carbon decreases that is transported with the groundwater into the lake.

Photosynthesis in freshwater
In this section, I will present the challenges aquatic plants meet in a freshwater system, and describe
some adaptation strategies in general. This will be exemplified by several plant species, especially water lilies, but also submerged and emergent plants. Consequences for radiocarbon dating and $^{14}$C ages of recent plants from the literature will end this section.

CO$_2$ concentrations in air at sea level and in pure water are roughly the same. Aquatic plants have the advantage that there is only 1/20 of the vol% O$_2$ in water than in air, but the larger disadvantage that the coefficient of molecular diffusion is much lower in a liquid than in a gaseous medium. This larger diffusion coefficient limits the rates of assimilation for aquatic plants. It is indicated by a lower coefficient of discrimination against $^{13}$C in water plants (Hutchinson, 1975; Keeley and Sandquist, 1992). The diffusivity $^{13}$CO$_2$ is only about 1% less than that of $^{12}$CO$_2$, whereas a considerably greater difference of about 2-3% may be expected in the rates of chemical reactions (Hutchinson, 1975; Park and Epstein, 1961). Aquatic plants have three strategies for coping with the low diffusion coefficient:

- increase surface-to-volume ratio, e.g. the yellow water lily Nuphar lutea has thinner leaves than would be possible for terrestrial plants
- use HCO$_3^-$ in addition to or instead of CO$_2$, as the HCO$_3^-$ concentration in most waters is substantially higher than the CO$_2$ concentration
- floating leaves utilise atmospheric CO$_2$

The HCO$_3^-$ is, as well as the released hydroxide ions OH-, balanced by calcium ions when taken up by the plant.

The utilisation of atmospheric CO$_2$ by floating leaves is plausible as floating leaves have stomata, pores for gaseous exchange, on the upper side (Hutchinson, 1975). Additionally, it was discovered that the wetting of the surface of floating leaves reduced the rate of photosynthesis in Nuphar polysepulum (Brewer and Smith, 1995). The assimilation of atmospheric CO$_2$ must therefore play a substantial role for this species. Aquatic plants are also able to take up carbon through their roots and air-filled spaces in their stems and leaves (Olsson and Kaup, 2001). This is an advantage as the concentration of interstitial CO$_2$ in the sediment often is 100 times as great as in the lake water (Olsson and Kaup, 2001). The maximum photosynthetic yield in C4 plants is obtained at 30-40°C, so Hutchinson (1975) deemed it unlikely that C4 photosynthesis occurs in submersed macrophytes. In contrast to Hutchinson (1975), another study found all kinds of photosynthesis pathways in freshwater plants: C3, C4 and CAM (Keeley and Sandquist, 1992).

The $\delta^{13}$C value of a plant depends on which DIC species it utilises, but also on factors such as DIC availability and temperature. If bicarbonate availability is limited, the fractionation between bicarbonate and the plant cell will be less than the typical 18-19‰ (Olsson and Kaup, 2001), and results in more enriched $\delta^{13}$C values. This effect is more severe at higher temperatures, because the growth rate is higher (Olsson and Kaup, 2001), and in standing water, because the carbon pool is limited for the individual plant (Keeley and Sandquist, 1992). Higham et al. (2010), for example, found $\delta^{13}$C values of -19.7‰ and -19.8‰ for water HCO$_3^-$ and unidentified aquatic plant matter. Water HCO$_3^-$ and aquatic plant had thus almost identical $\delta^{13}$C values, so fractionation did not occur at all, and the carbon pool must have been very limited. CO$_2$ in the water has, in equilibrium with HCO$_3^-$ at 10°C, ca. 9.5‰ lighter values than the HCO$_3^-$ (Emrich et al., 1970; Romanek et al., 1992). This leads to lower $\delta^{13}$C values of the plants. The suitability of $\delta^{13}$C values of aquatic plants for identifying CO$_2$ or HCO$_3^-$ assimilation is thus limited, as low $\delta^{13}$C-values can be caused by the assimilation of HCO$_3^-$ including large fractionation, or by the assimilation of CO$_2$ without fractionation. Enriched $\delta^{13}$C values, however, always indicate HCO$_3^-$ assimilation. As an example, two specimens of Myriophyllum from an Estonian lake had $\delta^{13}$C values of -17.8 and -12.2‰. These $\delta^{13}$C values are high and are expected to be the result of HCO$_3^-$ photosynthesis. However, the plants must also be able to utilise CO$_2$, because when Myriophyllum are grown commercially, they are often grown in soil and humid air. In fact, many aquatic plants can utilise both DIC species (Osmond et al., 1981).

It is expected that emergent and floating leaves have terrestrial radiocarbon ages, while submerged plants reflect the reservoir age of the DIC. One of the earliest studies of the freshwater reservoir effect confirmed this expectation. The “materials forming entirely within fresh-water bodies” had the same $^{14}$C concentration as the dissolved bicarbonate (Broecker and Walton, 1959), and aquatic moss was affected by a reservoir effect as well (MacDonald et al., 1987). Emergent plants were found to have $^{14}$C contents in equilibrium with the atmosphere (Deevey et al., 1954). Also Nuphar lutea from two Estonian lakes, collected in 1990, showed the expected behavior, with floating leaves having terrestrial radiocarbon ages (Olsson and Kaup, 2001). Already in 1953, however, Anderson et al. (1953) noted that “…the specific activity of water plants may depend on whether they photosynthesize CO$_2$ from the air and CO$_2$ dissolved in the water, or they photosynthesize bicarbonate.”
A study by Olsson et al. (1969) revealed some discrepancies: 5 samples of aquatic plants were collected in 1966, one sample of aquatic moss in 1968, and radiocarbon-dated. Comparison with $^{14}C$ measurements of the contemporaneous atmosphere (Olsson and Klasson, 1970) yielded estimates of the reservoir age. For representing the growing season best possible using the available atmospheric samples, for aquatic plants collected in 1966, the average of the atmospheric samples from September 1965 and August 1966 was used. The pmC of the aquatic moss was compared to samples of atmospheric CO$_2$ collected in April 1968 and May 1968. The emergent sedge Carex elata has a reservoir age of 470 $^{14}C$-years, a sample of floating plants 1180 $^{14}C$-years and three samples of submerged plants and Characeae had reservoir ages between 1060 and 2000 $^{14}C$-years. Floating and submerged plants do thus not have different reservoir ages, and the reservoir ages are high and variable (Olsson et al., 1969). An interesting case is the moss collected in 1968, because it has a negative reservoir age of -430 $^{14}C$ years. This is apparently a consequence of bomb $^{14}C$ in the lake (see section 2.1.3). The decrease of $^{14}C$ concentration after the end of atomic bomb tests is faster in the atmosphere than in the lake.

In a study of freshwater sediments, another interesting discrepancy was discovered. The “true” ages of all of these samples were so high that they had not been influenced by the bomb pulse or the Suess effect. Remains of Potamogeton spp. and Nuphar lutea showed a full hardwater effect of about 500 years, while a sample of Nymphaea alba had terrestrial radiocarbon age (Tornqvist et al., 1992). Consequently, Nymphaea alba has been used for constructing an age model, along with terrestrial samples (Hamm arlund et al., 2003), without even mentioning the possibility of a reservoir effect.

Both water lilies, N. lutea and N. alba, have floating leaves. They are thus expected to have the same reservoir age. Neither the floating and submerged leaves of N. lutea nor N. alba utilise HCO$_3^-$ (Smits et al., 1988), and they are thus expected to be able to utilise atmospheric CO$_2$. Both water lilies are eu-ryionic species. N. lutea was found in 12% of acidic lakes (pH 4.4-6.9), 43% of variable or neutral lakes and 68% of alkaline (pH 7.0-9.0) lakes in Denmark. N. alba was found in 18% of acidic lakes, 29% of variable or neutral lakes, and in 63% of alkaline lakes (Hutchinson, 1975). Common for both species is also the fact that, in early spring, they develop water leaves from the apices of the rhizome (the root stock in which they store nutrients from the previous growing season, see below). Water leaves are very thin, lack stomata and can even persist throughout winter when the water does not freeze. The floating leaves are formed in late spring and summer, are 4 to 4.5 times as thick as the water leaves and have stomata on their upper side. However, both water and floating leaves develop their characteristics underwater in similar environments (Hutchinson, 1975). The early water leaves of Nymphaea are less numerous and less persistent than those of Nuphar. Late in the season, Nymphaea may also form emerging leaves. The age difference between the two water lily species has been explained by the fact that Nuphar has more submerged leaves than Nymphaea so the CO$_2$ utilised by Nuphar might to a larger extent be derived from carbonate instead of from the atmosphere (Adams, 1985). However, as both species are fairly similar with regards to photosynthesis, I would suggest not to treat N. alba as a species that is totally unaffected by reservoir effects. For N. lutea it had already been shown that in some cases it shows a full freshwater reservoir effect (Tornqvist et al., 1992), in other cases a terrestrial $^{14}C$ age (Olsson and Kaup, 2001).

Also the stem of this recent Nuphar lutea leaf with the terrestrial $^{14}C$ age was dated. Surprisingly, it had higher $^{14}C$ levels than the leaf (Olsson and Kaup, 2001). This was interpreted as a memory effect, because the plant grew during the decreasing part of the bomb pulse (section 2.1.3). The rhizomes of water lilies store nutrients from the previous growing seasons to provide them for growth in early spring. They have been widely used as human food (Hutchinson, 1975, and references therein; see also section 6.2.2). The primordia of all the leaves and flowers of Nuphar are formed the year before they appear as functional organs (Hutchinson, 1975). The stems grew thus utilising nutrients stored in the root stock, so these submerged parts of the early growth incorporated carbon from the last several years, containing more bomb-$^{14}C$ (Olsson and Kaup, 2001). In Lake Långa Getsjön, the floating leaves of Nymphaea alba had slightly lower $^{14}C$-activity than the water leaves (the leaves of the same plant that were under water) (Olsson and Kaup, 2001). This might indicate a memory effect as well, because the water leaves depend to a higher degree on nutrients from the rhizome.

In an overview of several studies, Birks (2001) divided aquatic macrophytes into two groups, depending on hardness of the water and carbon source for photosynthesis (see table 2.1). However, this information cannot be used directly for assessing the possibility of a hardwater effect: while all the plants from the first group are likely to show a hardwater effect, the same is true for the submerged species of the second group, including N. lutea.
Aquatic plant species that utilise HCO$_3^-$ and are characteristic of hard, carbonate-rich water
- Ceratophyllum demersum
- Myricophyllum alterniflorum
- M. spicatum
- many Potamogeton spp.
- Rumunculus aquaticus
- Zannichellia palustris
- Characeae algae

Aquatic plant species that utilise CO$_2$ and are characteristic of soft, acidic water
- Hippuris vulgaris
- Isoëtes lacustris
- Naias flexilis
- Nuphar lutea
- Potamogeton natans
- P. polygonifolius
- Subularia aquatica
- Many mosses

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<tr>
<th>Aquatic plant species that utilise HCO$_3^-$</th>
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<td>Zannichellia palustris</td>
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<td>Characeae algae</td>
<td>Subularia aquatica</td>
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<td>Many mosses</td>
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Table 2.1: Aquatic plants sorted by carbon source for photosynthesis, CO$_2$ or HCO$_3^-$. Compiled by Birks (2001), based on information from Smits et al. (1988); Adams (1985); Keeley and Sandquist (1992); Spence and Maberly (1985).

An early study of δ$^{13}$C values in freshwater plants found a simple relation, similar to Broecker and Walton (1959). Floating leaves had $^{13}$C ratios similar to terrestrial plants, which was interpreted as the utilisation of atmospheric CO$_2$, while the organic carbon of submerged plants was enriched in proportion with the hardness of the water (Oana and Deevey, 1960). The greater the water hardness, the greater the DIC fraction that derives from dissolved limestone with δ$^{13}$C≈0. However, greater water hardness can have the opposite effect and lower the δ$^{13}$C values of aquatic plants. In hard water, the bicarbonate reservoir is much larger. CO$_2$ can be supplied at a faster rate, which leads to maximum fractionation, and thus maximum discrimination against $^{13}$C. This was observed by Stuiver (1975). This is supported by the study of organic lake sediments from two carbonate rich lakes. Hammarlund (1993) found that when the CaCO$_3$ content was zero, the δ$^{13}$C values were high (up to -23%/permil). The water hardness has undoubtedly an influence on δ$^{13}$C values of water plants, but as it can both increase or decrease the δ$^{13}$C values, it cannot be used to predict the δ$^{13}$C of water plants. Also the great range of δ$^{13}$C values in a freshwater system makes such predictions impossible. In a single lake’s water plants, variations of up to 10%/permil can occur (Stuiver, 1975). Productivity and climate, such as the transition from Pleistocene to Holocene, are other factors that can control δ$^{13}$C values. Hammarlund (1993), for example, measured -23.2%/permil for sediment samples older than 10000 $^{14}$C BP, and -28.2%/permil for Holocene samples.

### 2.4 Methods for pottery analysis

The analysis of pottery in the context of this study is radiocarbon dating and reconstruction of pottery use. The reconstruction of what was cooked in the prehistoric pots indicates whether a reservoir effect has to be expected when $^{14}$C dating a food crust. Modern food crusts which I had produced in copies of prehistoric pottery could be used as a reference material for testing different methods.

#### 2.4.1 Dating of pottery

Pottery is one of the most important materials in prehistoric archaeology. The reasons are summarized by Clark (1976):

In early times it was primarily a local product, it was made in abundance, it survived relatively well and although representing only a single craft, which may in some cases have played a relatively unimportant role, the product was complex and involved a number of variables, including composition, building, firing and shape as well as the technique, form and disposition of ornamentation.

This section focuses on the relevance of pottery, and the problem of accurate dating, to present-day researchers. A summary of the importance of pottery for prehistoric people is given in section 5.3. Here, the principles of pottery dating are summarized and followed by some examples for radiocarbon dating of prehistoric pottery.

The oldest method of pottery dating uses pottery style and technique to build up chronologies. A precondition for this dating method is that different pieces of pottery, looking the same and made and decorated in the same way, are contemporaneous. Another is that changes only occur gradually, so that it is possible to build up a so-called “typological sequence”. Apparently, people in certain cultures and in certain times all used the same techniques and
shapes for producing pottery, although many different kinds of pottery would serve the same purpose. As Hayashida (2003) remarks, “There may be many ways to make a sturdy cooking pot given available materials but the particular clays chosen and the techniques used to form, finish, and fire the vessels are linked to such diverse factors as the organisation of the potters, their social identity, the perception of different raw materials and fuels, and the integration of pottery-making with other activities”. The typological method is the least expensive one and done by archaeologists themselves so that the result is immediately available. However, this method only provides relative datings and is subjective. For absolute datings, other scientific methods have to be applied.

Thermoluminescence (TL) dating is one example. It dates the moment of the last heating of a sample containing minerals, as the firing of pottery. A thermoluminescence signal builds up as a mineral is exposed to natural radioactivity. The TL signal is zeroed when the mineral is heated. When zeroing a mineral in the laboratory, a measurement of the thermoluminescence signal, the amount of light emitted by the mineral, is a measure for the time since the last zeroing. The advantage of TL dating is that it avoids radiocarbon reservoir effects or the old wood effect, and that it is not as expensive as AMS. Limitations are that a sherd “may have been accidentally reheated after original firing”, that it “may not have been completely zeroed in ineffective firing” and that “some ceramics do not hold a TL signal” (Johnson et al., 1986).

However, the following explanations only deal with radiocarbon dating for age determination of pottery, as this is the method I used.

The main restriction when trying to radiocarbon-date pottery is the limited extent to which carbon can be found in pottery. Radiocarbon dating of pottery was first made possible with the introduction of AMS (see Feathers, 1993). Conventional $^{14}C$ dating (with beta-decay-counting) could only be applied to associated samples of another material, for example charcoal, or implied the destruction of large quantities of sherd material (Johnson et al., 1986). Other problems originate from the variety of possible carbon sources and the different points in time they belong to: carbon originally present in the clay, carbon added as organic temper, carbon from soot deposits made during manufacture or use, carbon from food residues, and secondary carbon contamination after deposition (DeAtley, 1980; Feathers, 1993). All these different carbon sources may have different ages (Hedges et al., 1992). Pottery normally consists of 50 to 70% clay. Carbon originally present in that clay has normally infinite ages, although it can be younger (a few thousand years) when it closely underlies surface vegetation. In each case, it tends to increase the apparent age of the potsherd. Quarried clays may contain up to 20% organic matter which can have geological ages (Hedges et al., 1992).

There are two datable moments when analysing pottery: The firing (i.e. production) and/or last heating as well as the last use for processing food.

20 to 50% of a potsherd consist of temper which is likely, but not exclusively, contemporaneous with the production of the pottery. If consisting of organic matter, temper is generally useful for dating. Though being useful for dating, it is not very probable that enough temper survives the firing process. Gabasio et al. (1986) studied modern pottery with known composition of clay (known carbon content), different temper and different amounts of organic admixture. Experiments with reconstructed neolithic kilns showed that the addition of up tp 10% organic matter did not change the carbon content of the pot after firing. Often only imprints of burnt temper particles remain. But even if present, organic temper is hard to separate from other organic material that was in the clay long before it was formed and burned. In the case of the pottery examined in this thesis, granite chippings were used as temper. The temper provides thus no carbon contemporary with the pot for radiocarbon dating.

Carbon from soot deposits made during manufacture or cooking is also regarded as useful for dating although the old wood effect has to be taken into account. The more porous a pottery is, the more soot can be deposited during firing. Also the use of primitive kilns enlarges the fraction of carbon deposits in the pottery, because pottery in primitive kilns is in direct contact with the fuel. Generally, the fire in primitive kilns is fed by wood or dry grass so that a lot of soot develops. It is therefore expected that prehistoric pottery contains enough carbon from the fire to date the firing process, whereas more advanced pottery from historical times, fired without direct contact with the fuel, is expected to be difficult to date (Gabasio et al., 1986). However, pottery from historic epochs can normally be dated more easily and precise by style than by scientific methods.

Carbonaceous compounds such as humic acids can be introduced from the burial context. Although this is regarded as contamination, it possibly tends to reflect the date of the burial stratum and often does not seriously alter the dating of the sherd. Bacterial activity has also to be taken into account if the sherd was buried in an organic-rich deposit (Hedges, 1992). Bacteria, though, normally do not change the
isotopic composition of the carbon to a significant extent because they use carbon from the sample instead of introducing carbon from other sources.

The last use for processing food can be dated when a crust of charred material is found on the sherd. As a pot with a thick, charred crust is not best suited for the preparation of well-tasting food and as it is impossible to completely clean such a porous pot, one can assume that the pot was not used much for cooking after the formation of the crust. Apart from its potential for dating, the existence of food crusts provides the knowledge that the examined type of pottery was used for the processing of food and not, for example, only for carrying or storing water (Andersen and Malmros, 1984). Because the sherds appear thick, fragile and porous when excavated, it was doubted for some time that the pots had been suitable for cooking. Klingen (1932) for example tried to boil water in rebuilt Ertebølle pots, but he did not succeed because the water was evaporating through the pores of the pot already at 70-90°C. Therefore, he concluded that the pots were only used as salterns for sea water. Ertebølle pots that were found in the inland, far away from supplies of sea water, contradicted this interpretation (Mathiassen, 1935). Later experiments in which starch or fat had been added to the liquid in the pot also disagree with Klingen’s conclusion: the pores of the pot were sealed with starch or fat so that the content could be heated up to the boiling point (Andersen and Malmros, 1984). In contrast to that, a charred crust on the inside of a pot can have a completely different reason, as ethnographical observations indicate: In Western Sudan, simple clay pots have been waterproofed by filling them with grass or straw before firing them upside down. The soot layer in the pots prevented water from soaking through the pores so that the pots were suitable for boiling water (Håland, 1979). However, as our experiments showed, it is neither necessary to add starch or fat nor to waterproof with soot, when boiling water in Ertebølle pottery (section 6.3).

On many pots of the Late Mesolithic Ertebølle culture, crusts of charred organic material are preserved, especially in coastal and bog areas (e.g. Andersen and Malmros, 1984). In the material from Schleswig-Holstein, food crusts from pots at coastal settlements are always thicker than those from inland sites, an observation that is not yet understood (pers. comm. S. Hartz 2007). A possible reason is the better preservation environment for organic samples at coastal sites. The thickest crusts occur on the inside of the pots, especially in the bottom half of the pots. Crusts on the upper outside of the pots are explained to come from a liquid content boiling over, for example a soup. The reason for the absence of such crusts on the outside of the bottom half of the pot could be that the food remains were completely charred away by the hearth fire (Andersen and Malmros, 1984). Crusts on the outside of the pots could also come from soot, as explained above.

One example for the dating of food crusts from the EBK is the submarine settlement Tybrind Vig on the western coast of the island Fyn in Denmark. The pottery at this site was embedded in the gyttja of the waste zone and is therefore well preserved. The site is radiocarbon dated to 4400-3200 BC (in uncalibrated 14C-years), whereas the pottery is from 3700-3500 BC (in uncalibrated 14C-years) (Andersen and Malmros, 1984). The calibrated date for the site is approximately 5400-4000 BC and for the pottery approximately 4500-4350 BC.

A possible hardwater effect on pottery has been shown by Fischer and Heinemeier (2003). Pottery dating from Estonia has in one case given a date that was 1000 years older than expected (Kriiska et al., 2005). This dating may be correct and the archaeological assumption may have to be corrected, but it is also possible that the hardwater effect contributed to the high age of the pottery which was found on a site at a river bank (Kriiska et al., 2005). Nakamura et al. (2001) report ages as high as 15,710-16,540 cal BC for the earliest Japanese pottery. It had been assumed before that the use of pottery started with the Jomon Culture in the Holocene after a series of climatic fluctuations. The AMS dating of pottery, though, suggests that the first pottery was already made during a cold climate period “predating such climatic fluctuations by about a millennium”. It would be interesting to examine this pottery closer to find out if it also had been influenced by the hardwater effect or if those surprisingly high radiocarbon ages also correspond to high historical ages. Up to now, the younger ages of charcoal samples have been explained with the assumption that these charcoal pieces really are younger and have been anthropogenically or naturally mixed into the layers in which the pottery was found (Nakamura et al., 2001).

Segerberg et al. (1991) extracted protein for radiocarbon dating from food crusts from some Swedish sites. For obtaining one milligram carbon, 1 gram food crust is needed from which proteins are extracted with the “Lowry”-method. Amino acids are split using high performance thin layer chromatography (HPTLC). From the resulting 3 mg amino acids, 1 mg carbon can be gained. The surprising result of the amino acid extraction was that the amino acid which normally is most abundant in all nutritives, glutamine, was totally absent on one sherd and only
detectable on another one. Alanine, though, a simple non-essential amino acid, was found in large amounts on another sherd. This can be explained by the fact that alanine is the simplest of all amino acids and large quantities of it are present in strongly deteriorated products. The amino acid composition of the potsherds is thus an indicator for the fact that they are broken down by natural or man-made processes.

Another attempt is the extraction of lipids for radiocarbon dating from the entire sherd. Lipids absorbed in the ceramic matrix are assumed to be well protected from degradation and contamination (Heron et al., 1991). Hedges et al. (1992) tried this using Soxhlet extraction in acetone. Many of the archaeological sherds they examined contained extractable lipids at the level of 0.02 to 0.4% and seem to be a good dating material. Lipids are rather immobile and lipid concentrations in soils are low so that little exchange between sherd and burial context can be expected. Nevertheless, only 3 out of 7 examined sherd provided reasonable (not necessarily accurate) lipid ages.

Stott et al. (2001) also used lipid extraction for radiocarbon dating of potsherds but they extracted different fatty acids from the sherd material. Stearic (C18:0) and palmitic (C16:0) acid and the C18:1 unsaturated acid provided high enough concentrations for radiocarbon dating when examining potsherd samples of about 10 g. After extraction, the lipids were derivatized and purified. Gas chromatography (GC) was used for extracting the single fatty acids. This method proved to be very time-demanding: To obtain sufficient material for precise dating repetitive, accumulating, GC separation was necessary. About 100 runs were needed for each sample. The radiocarbon ages obtained for the fatty acids were variable and, in the case of C16:0, systematically too young by 100-150 years. In a later study, C18:0 radiocarbon ages agreed well with the archaeological context. However, C16:0 was still too young. This was explained by contamination from the burial environment; C16:0 is the most dominant fatty acid in soil organic matter in this carbon number range (Stott et al., 2003). However, the method was developed further, and radiocarbon dates of C16:0 and C18:0 agreed well with each other and with the dendrochronologically dated context of a Neolithic site (Berstan et al., 2008).

2.4.2 Stable isotope analysis of food, human bone and pottery

When reconstructing the ingredients from a food crust on pottery, as will be attempted in chapter 6, the isotopic ratios of the possible ingredients cannot be compared directly to the food crust. Fractionation during the processing, e.g. heating, of the food have to be considered. Additionally, isotope values of bone collagen cannot be used as a proxy for the flesh used in cooking. The bones and food crusts from an excavation are not directly comparable. For example, Katzenberg et al. (1995) found that fish flesh is 2-4% more negative than bone collagen. Lanting and van der Plicht (1998) measured a difference of 1.5% between flesh and bone collagen of pike-perch. In addition to this inherent differences, changes in habitat can possibly lead to differences as well. Bones reflect the diet of a longer period, and the flesh only recent diet (Lanting and van der Plicht, 1998).

An isotopic shift has also be considered in diet reconstruction by stable isotope measurements of human bone: Katzenberg et al. (2000) measured δ13C values of human bones from the mid-1800s and compared them to the historically recorded diet of these people. δ13C values of ingredients used at that time were measured. They discovered a difference of δ13C between diet and bone of about 5.6%. Modern foods are slightly more negative due to burning of isotopically light fossil fuels. The difference between the original diet and bone is thus assumed to be slightly less than 5.6%. Lanting and van der Plicht (1998) suggest the following mean values for the bone collagen that can be expected in 100% diets of the following categories: δ13C=-21% for a pure C-3 vegetables-diet, δ13C=-18 and δ15N=+8 % for flesh of C3-herbivore-diet, δ13C=-13 and δ15N=+18% for marine diet, δ13C=-24 and δ15N=+16% for freshwater (river) diet and δ13C=-20 and δ15N=+16% for a freshwater (lake) diet. In addition to differences in δ13C values between bones and flesh, it should be taken into account that fat is considerably lighter in δ13C than lean meat (Bonsall et al., 1997; Park and Epstein, 1961; Parker, 1964; DeNiro and Epstein, 1977).

Modern domesticated animals can have higher δ15N values than the typical 1-6‰ of their wild ancestors as they can have more “omnivorous” feeding patterns. Similar effects can already be expected for prehistoric domesticated animals as a result of feeding with e.g. pondweed or human food refuse (Bonsall et al., 1997; Schwarcz, 1991). The δ15N values of crops can increase by up to 3.5‰ due to manuring (Fraser et al., 2011).

Several studies have examined changes in δ13C and δ15N during cooking and other preparation methods of different foodstuffs. There is no significant difference in isotope values of plants and heated plants (Hastorf and DeNiro, 1985). The δ13C variation is less than 1‰ when heating (boiling and roasting) maize
cobs, sunflower seeds, agave leages and Pachyrrhizus tubers (Marino and DeNiro, 1987). Other authors found that heating has a small effect on $\delta^{13}C$ values. In some cases, mixing of ingredients has an additional effect. Differences are less than 1.5% and not always in the same direction, e.g. carrots from -28.9‰ (raw) to -27.7‰ (cooked), beef: -24.3‰ (raw) to -24.4‰ (cooked) (Katzenberg et al., 2000; Abonyi, 1993). $\delta^{15}N$ values were analysed in another series of food preparation: Privat et al. (2005) measured $\delta^{15}N$ of milk, kefir, yoghurt and cheese (fresh, 2 months, and 14 months old) and did not find any significant isotopic alteration relative to the original milk from which they were made. Baking at 200°C and boiling in dem. water, each for half an hour, also had very little effect on various ingredients Bonsall et al. (1997).

Boudin et al. (2009a) tested a combination of thermal and microbial degradation by cooking food until charred and burying it in compost soil. The $\delta^{13}C$ values of hazelnut, wild boar and bream did not change, but the $\delta^{15}N$ value increased by 1% thermal degradation. A deer sample had a larger spread of $\delta^{13}C$ values and a 1‰ lower $\delta^{15}N$ value.

The few studies presented here did thus not find significant changes in isotopic ratios when processing food.

### 2.4.3 Infrared spectroscopy

Infrared spectroscopy is based on the fact that infrared radiation can excite vibrations of molecules. The excitation frequency is characteristic for functional groups. It is thus possible to identify the structure and components of a sample by measuring an infrared absorption spectrum. In an infrared spectrometer, an infrared beam passes the sample, and a detector determines the intensity of the transmitted beam. Modern infrared spectrometers are using the principle of Fourier-Transform IR spectroscopy (FTIR). The source of IR radiation is polychromatic (a black body). The IR light passes an interferometer before entering the sample. One of the interferometer’s mirrors is movable. A He-Ne-laser acts as a reference light source. It is also guided through the interferometer to exactly determine the mirror’s position. The two IR beams in the interferometer interfere depending on their frequencies and on the mirror’s position. The resulting interferogram contains one big maximum where both mirrors had the same distance to the beam splitter and where all frequencies interfered additively. With a Fourier-transformation, an infrared spectrum is calculated from the interferogram. FTIR is a comparatively cheap, easy and fast technique and it is possible to construct compact, transportable FTIR spectrometers for on-site use. It is used in archaeological science for a variety of applications (see examples below). It would be well suited for screening food crust samples, for example to assess the presence of lipids or proteins, or the amount of clay present in the sample. Clay would not disturb a $^{14}C$ or $\delta^{13}C$, $\delta^{15}N$ measurement, but necessitates bigger sample sizes for pretreatment and combustion.

The presence of absorptions at the following wave numbers (in cm$^{-1}$) indicates the following substances in archaeological samples:

- 565 phosphate (Stiner et al., 1995)
- 858, 1435 and 713: aragonite
- 874 carbonate (Stiner et al., 1995)
- 1035: major clay absorption, can be shifted to 1040-1050 cm$^{-1}$ due to small amounts of the phosphate mineral dahllite (Yizhaq et al., 2005)
- 1033 (strong), 535 and 472:clay
- 1032 is the Si-O-Si peak, typical of clay minerals
- main absorption at 1035, rel. prominent at 535: non-altered clay minerals
- broad absorption at 1040: polysaccharides or humic acids (Weiner and Bar-Yosef, 1990)
- 1085, doublet around 780, and 464: quartz
- 1097, doublet around 790 and 473:opal, the mineral component of siliceous plant phytoliths
- 1300 carbon, disordered material outside the graphite layers
- 1384 nitrate from the soil (Yizhaq et al., 2005)
- 1456, 1417, 872 carbonate (Stiner et al., 1995)
- 1600 graphite
- 1650 water (Weiner and Bar-Yosef, 1990)
- amino acids: 1563 amide I, 1539 amide II, 1456 proline of collagen (Stiner et al., 1995; Yizhaq et al., 2005) (with decreasing height, Weiner and Bar-Yosef 1990)
- 1718 to 1595: charcoal
- 2361, 2334: CO$_2$ peaks
- peaks just before 3000: organics like CH$_2$, CH$_3$

The exact wave number of an absorption band can give information about the proportion of different substances, e.g. saturated, mono- or polysaturated acyl groups in edible oil and lard (Guillén and Cabo, 1997).

As an example, figure 2.14 shows the infrared spectrum of pure charcoal. The application of FTIR spectroscopy in archaeological science will be discussed below.

### Sample preparation

In all the works regarded here, the sample was powdered, mixed with KBr, which is transparent for infrared radiation, and pressed into a pellet using a
2.4. METHODS FOR POTTERY ANALYSIS

Hand press or automated press (Figures 2.15, 2.16 and 2.17). The amounts of sample and KBr used in the different studies vary. The range of sample masses is between few 10 μg and 0.3 mg, while few mg to 80 mg of KBr were used.

Schiegl et al. (1996) mixed 0.1 mg or less ash sample with 80 mg KBr. For the classification of calcites, Chu et al. (2008) used 0.3 mg powdered sample and 40 mg KBr. For analysing sediments, 0.1 mg powdered sample were mixed with 80 mg KBr (Shahack-Gross et al., 2005). The same amounts, or even less sample, were used by Berna et al. (2007). For my samples (section 6.5.2), the amount was chosen by visual judgement, covering the tip of a spatula. The spectra are typically collected between 4000 and 400 cm$^{-1}$ and have a resolution of 4 cm$^{-1}$.

**IR spectroscopy and archaeological science**

In the following, I will describe the possibilities of IR spectroscopy to identify and characterise a sample’s content. I will use examples from recent research to illustrate the archaeological questions IR spectroscopy can answer.

IR spectroscopy can give information about the type of calcium carbonate polymorph and the extent of atomic order. That can be used to identify geologic, biogen or anthropogen calcite (Chu et al., 2008). The reason is that the high temperatures used in the production of e.g. plaster (“anthropogenic calcite”) introduce disorder into the calcite crystal lattice. This information is also useful for $^{14}$C dating of plaster and mortar, as one needs to know the origin of the $^{14}$C for correctly interpreting the data (Chu et al., 2008). Additionally, the degree of weathering can be quantified with IR spectroscopy of calcite. IR spectroscopy can also be useful for much older periods. At palaeolithic sites, it is desired to be able to identify ash, as this is an indicator of human activity. Fresh wood ash consists mainly of calcite. It is formed by the decomposition of calcium oxalate crystals followed by rehydration and carbonation to CaCO$_3$ (Schiegl et al., 1996). There are five stages in ash genesis which can be identified with IR spectroscopy. First, the ash is mainly composed of calcite, then of dahlilite, and then of montgomerite. In the fourth stage, the ash contains leucophosphate, and finally, only siliceous aggregates are present (Schiegl et al., 1996). In a totally different context, in a Phoenician monumental building, IR spectroscopy helped to show that the white “floors” found in the sediments actually were phytolith layers which indicate that the building, amongst other
spectroscopy and other techniques serve as a quality not reliably diagnose burning on prehistoric bones. IR and fossilation partly overlap. IR techniques did thus crystallinity of bones altered by weathering, burning, et al., 1995). They found out that the signatures of tion band to the phosphate absorption band (Stiner et al., 1995) used the dahlite (carbonatedapatite) splitting factor to estimate the crystallinity. In their study of burned bones, they estimated fur- thermore the relative carbonate content of the min- eral phase from the ratio of the carbonate absorp- tion of the relative sizes of the crystals as well as the extent to which the atoms in the lattice are or- dered. The crystallinity of the carbonate apatite crys- tals is reflected in the extent of splitting between two of its IR-absorptions (Weiner and Bar-Yosef, 1990). Stiner et al. (1995) also used the dahlite splitting factor to estimate the crystallinity. In their study of burned bones, they estimated fur- thermore the relative carbonate content of the min- eral phase from the ratio of the carbonate absorp- tion band to the phosphate absorption band (Stiner et al., 1995). They found out that the signatures of crystallinity of bones altered by weathering, burning, and fossilisation partly overlap. IR techniques did thus not reliably diagnose burning on prehistoric bones. IR spectroscopy and other techniques serve as a quality control for $^{14}$C dating in the study of Yizhaq et al. (2005). They used the IR splitting factor for a quality control of bone, while the purity of the charcoal samples was assessed via IR-measurements of the clay and carbon contents.

In chapter 6, I will introduce another archaeological material to this collection: food crusts on pottery.

2.4.4 Lipid analysis and other biochemical techniques

Fatty acids are a class of lipids. They are the principal constituents of food fats and oils (Heron et al., 2007). Fatty acid analysis of prehistoric pottery has a long tradition (e.g. Condamin et al., 1976; Condamin and Formenti, 1978; Mathiassen, 1935). The first analysis on Ertebølle pottery from Denmark was performed in 1935 by Einar Biihnann and K. A. Jensen, Copenhagen. They could show, amongst others, the presence of fatty acids with 16 to 18 carbon atoms in shal-

low ceramic bowls. These analyses agreed with the archaeological interpretation that the bowls had been used as blubber lamps (Mathiassen, 1935; Van Diest, 1981).

GC-MS (gas chromatography - mass spectrometry) can be used to identify lipid biomarkers. The molecules are separated and their masses are measu-
red, GC-C-IRMS (gas chromatography - combustion - isotope ratio mass spectrometry) furthermore measures the $\delta^{13}$C values of individual fatty acids (e.g. Craig et al., 2007, 2011). Certain fatty acids are characteristic for certain resources. Stable isotope values of individual fatty acids can further distinguish the food sources.

Pottery is often dominated by C16:0 and C18:0 fatty acids (e.g. Dudd and Evershed, 1998; Heron et al., 2007). However, many fatty acids occur in different foodstuffs and are thus not alone characteristic for a certain product. Brown and Heron (2005) gives some examples: While terrestrial animal fats and marine fats can easily be distinguished, there are similarities between fish oil and (terrestrial) seed oil, which both are depleted in saturated fatty acids in comparison with the unsaturated fatty acids. Three biomolecules have been proposed for the identification of fish oils in archaeological ceramics, C$_{16:1}$, C$_{20:1}$ and C$_{22:1}$. All these, however, can also be present in other sources, albeit in smaller amounts. C$_{22:1}$, for example, is also found in oat germ oil.

Certain fatty acids are indicators of heated fish oil, thus a direct demonstration for the processing of aquatic products (Hansel et al., 2004).

It should be kept in mind that not all fish processed in prehistoric pottery will leave a lipid signal. The soaking and cooking of salted and wind-dried coalfish, for example, resulted in a residue with amino acids and sugars, but little evidence for fatty acids (Brown and Heron, 2005).

In this study, the extraction of lipids from food crusts, instead of from the ceramic matrix, was tested. Furthermore, lipids that had been extracted from potsherds were radiocarbon dated. The results of these preliminary tests are presented in chapter 6.

In addition to lipids, proteins can sometimes be extracted from prehistoric pottery. Together with high levels of iron found in some food crusts, protein and lipid composition suggested that the prehistoric pottery from e.g. Tybrind Vig (cf. Andersen and Malmros, 1984) had been used for the production of a fermented porridge (Arrhenius, 1985; Arrhenius and Lidén, 1989).
2.4.5 Petrographic microscopy

The archaeological food crusts were homogeneous to the naked eye. No structures that could indicate their composition were visible. I investigated thus the possibility of using a petrographic microscope for inspecting the samples. With this method, details like spicules (e.g. from sponges), foraminifera, diatoms, oxalate or phytoliths can be discerned. Furthermore, clay, charcoal, calcium carbonate and quartz may be distinguished. An idea of the relative proportions of clay, calcium carbonate and organic material would be an advantage when pretreating the sample, e.g. for choosing the appropriate sample size. The identification of phytoliths in food crusts on Ertebølle pottery was e.g. performed by Arrhenius and Lidén (1989).

As the results have proven inconclusive (see section 6.5.3), I will not go into details with a literature review or with describing the method. In short, a petrographic or polarized light microscope has a polarizer filter in the light path beneath the sample. When a second polarizer filter is added above the sample, perpendicular to the first one, all light is blocked unless the sample contains anisotropies (i.e. birefringent components). When turning the stage with the sample, an anisotropic sample lights therefore up in the crossed filters. Furthermore, interference colours can be observed.

2.5 Summary

This chapter has provided the methodological background for the studies presented in this dissertation. Radiocarbon dating in theory and praxis as well as reservoir effects have been explained. Special emphasis was put on the freshwater reservoir effect, partly because it is highly complex, but also because it is in the focus of this paper.

Stable isotope measurements will supplement radiocarbon dating of various materials. $\delta^{13}$C will be measured in all materials that are radiocarbon dated, on the one hand for fractionation correction, and on the other hand to give additional information about the origin of a sample, e.g. terrestrial vs. marine. $\delta^{15}$N values will be measured in food to reconstruct the trophic level of the ingredient and distinguish plants from terrestrial herbivores and fish. $\delta^{15}$N values on organic matter in a fjord sediment will indicate processes like changes in land-use in the catchment. $\delta^{18}$O values in water DIC reflect precipitation dynamics, while $\delta^{18}$O values in mollusk shells and foraminifera from an estuarine environment are influenced by water temperature and salinity.

Additional methods from archaeological science were presented as they will experimentally be applied for food crust analysis.
Chapter 3

Methods

This chapter describes the specific methods used in this study. For general information on the radiocarbon dating and stable isotope analysis, see chapter 2.

3.1 Sample collection and pre-treatment

Water samples were collected in 0.5L dark brown bottles which were filled underwater up to the top, avoiding whirls, thus avoiding too much contact with atmospheric air. 3-4 drops of a solution of HgCl₂ (7 g per 100 ml) were used for preserving the samples, e.g. avoiding growth of algae which would consume DIC (dissolved inorganic carbon) and build up organic carbon. The samples were kept dark and cool until analysis. Modern aquatic macrophytes and animals were sampled alive. As many riverine mollusc species are protected by environmental legislation, it was chosen to collect shells of recently-dead individuals from the rivers. Material for AMS dating, shells and terrestrial plant remains, from the sediment core in the Limfjord (section 7) was retrieved by wet sieving. Archaeological samples were, in co-operation with archaeologists, chosen from the archives of the respective archaeological institutions.

3.1.1 Modern organic samples

Modern ingredients for food crust experiments, aquatic plants and animals were freeze-dried prior to analysis. There were no visible carbonate encrustations on the aquatic plants. HCl-pretreatment was therefore not considered necessary. From some recent fish bones, collagen was extracted, as this is the material used for analyses of archaeological bones (see below).

3.1.2 Charcoal, wood and food crusts

Archaeological samples were inspected with a stereo microscope. Visible contamination, such as sand or rootlets, was removed from the samples using a scalpel or tweezers. Archaeological charcoal and wood samples as well as plant macrofossils from the sediment core were pre-treated by the acid-alkali-acid method, with 1M HCl at 80°C for one hour, 1M NaOH at 80°C for at least three hours and lastly 1M HCl at 20°C overnight. Archaeological and experimental food crusts were under a stereo microscope carefully scraped off from the sherds with a scalpel. Pretreated like charcoal, but at 20°C instead of 80°C, and with 0.5 or 0.2 1M NaOH in case of frail archaeological food crusts. If a large proportion of the sample dissolved during the NaOH step, this so-called base soluble fraction was separated from the sample, precipitated with an excess of 1M HCl, boiled in demineralised water, and dried. The chemical pretreatment of the experimental food crusts is not necessary for removing contaminant, as these samples have not been buried in the soil, but for extracting chemical fractions comparable to archaeological food crusts after pre-treatment.

3.1.3 Bone

General considerations about the chemical pretreatment of archaeological bone samples are presented in chapter 2. The following method is used at the AMS ¹⁴C Dating Centre and was also applied to my samples:

1. clean the bone’s surface with a special drill (alternative: clean in demineralised water and ultrasound)
2. drill out 200 to 300 mg bone powder (alternative: smash and pestle a piece / pieces of bone)
3. decalcification
   (a) cool the bone powder to 5°C
   (b) add 1M HCl, also at 5°C

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3.14 Water DIC and shells

Water DIC was extracted by acidifying the water with 100% H₃PO₄ (85%), thus converting all carbonate and bicarbonate to CO₂. The CO₂ was extracted from the water by bubbling N₂ through it and was cryogenically trapped.

Mollusc shells are pretreated for radiocarbon dating and δ¹³C and δ¹⁸O measurement by removing possible organic remainders and the outer layer of shell carbonate. The shells are then acidified to yield CO₂. The procedure is summarized below.

1. ultrasonic bath, demineralized water, 2 minutes (less for brittle samples)
2. the outer parts of the sample are removed with 1M HCl: the sample is covered with demineralized water, then a specific amount of HCl is added, depending on the sample size, and is left until the reaction is finished (no more bubbles)
   - sample size ≥ 14 mg: the outer 20-25% are removed (40 μl HCl for every 10 mg of shell)
   - sample size ≥ 8 mg: the outer 10% are removed (20 μl HCl for every 10 mg of shell)
   - sample size < 8 mg: no HCl
3. 25 ml demineralized water with 7-8 drops of 0.25M KMnO₄, 16-20 hours at 80°C
4. 13-14 mg of pretreated shell are weighed out into a flask
5. 100% H₃PO₄ is added to the flask, but separated from the sample
6. after evacuation, H₃PO₄ is poured upon the sample and left overnight to react at 25°C, converting the shell’s CaCO₃ into CO₂

3.2 Radiocarbon Dating

Organic samples were converted to CO₂ by combustion in sealed evacuated quartz tubes containing 200 mg CuO. The CO₂ from acidification (water DIC and shells) and from combustion is converted to graphite with the H₂ reduction method (e.g. Vogel et al., 1984, see also section 4.3).

Most measurements were performed at the AMS ¹⁴C Dating Centre at Aarhus University (AAR-numbers). Some shells from the Limfjord sediment core were dated at the ¹⁴CHRONO Centre, Queen’s University Belfast (UBA-numbers). As the accelerator in Aarhus was out of action for extended periods, some ¹⁴C measurements had to be performed at other laboratories. However, chemical pre-treatment, data analysis, quality control and δ¹³C measurements were still performed in Aarhus, so these dates are also marked with AAR-numbers, irrespective of what
3.3 Stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$)

Bulk sediment samples for the determination of total organic carbon (TOC), total nitrogen (TN), $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios were pre-treated with 1M HCl at 60$^\circ$C to remove carbonate, washed with deionised water and freeze dried.

Organic samples for $\delta^{13}C$ and $\delta^{15}N$ measurements were weighed out into tin capsules. The required sample size of 35 $\mu g$ nitrogen and 100 $\mu g$ carbon corresponds to sample sizes between 200 and 250 $\mu g$ collagen. For food crusts, plants and sediment samples, larger sample sizes of up to 10 mg are required, depending on carbon and nitrogen content. These sample types have much larger C/N ratios than bone collagen. The samples’ CO$_2$ had thus to be diluted as the CO$_2$ peak otherwise would be too large for a measurement (overrange). The analyses were performed by combustion in a EuroVector elemental analyser coupled to an IsoPrime stable isotope ratio mass spectrometer at the AMS $^{14}C$ Dating Centre at Aarhus University. Most samples yielded enough material for doublet measurements. $\delta^{13}C$ values are reported as $\%$ VPDB, $\delta^{15}N$ values as $\%$ AIR. C/N ratios were derived from TOC and TN measurements and are presented in atomic units.

$\delta^{13}C$ and $\delta^{18}O$ of water DIC and shells were measured on a CO$_2$ aliquot from the radiocarbon preparation using a Dual Inlet IsoPrime stable isotope mass spectrometer (Figures 3.1, 3.2) at the AMS $^{14}C$ Dating Centre at Aarhus University. Measurements were performed relative to the internal standard material Carrare CaCO$_3$. $\delta^{13}C$ and $\delta^{18}O$ values are reported as $\%$ VPDB (Coplen, 1994) and were determined with a standard deviation of 0.05 $\%$ VPDB. $\delta^{13}C$ values of many organic samples were also measured with the Dual Inlet setup, especially when a $\delta^{15}N$ measurement would not have given additional information about the sample. These $\delta^{13}C$ values will be denoted (DI) in this study. $^{15}N$ is reported as $\%$ deviation from atmospheric air, AIR.
Chapter 4

Investigations of possible improvements of sample preparation techniques

The methods described in chapter 2 and 3 will be applied to, among other sample types, food crusts on pottery and samples from a sediment core. Both applications pose the same challenge: small samples. Therefore, two approaches have been tested to improve the handling of small samples. When a sample is so small that it yields less than about 0.5 mg carbon (mgC), stable isotope measurements are often omitted as all of the sample’s carbon is needed to secure optimal $^{14}$C dating. Valuable information is thus lost: As the $^{14}$C concentration can change due to fractionation, a δ$^{13}$C measurement is needed for correction. Furthermore, the stable isotopes $^{13}$C and $^{15}$N can provide valuable information about a sample’s origin (see section 2.2), and for example indicate the risk of a reservoir effect. In this chapter, I will thus describe my attempts to combine the extraction of carbon for $^{14}$C dating with stable isotope measurements. I will present some suggestions for improvements of the methods presented in chapter 2 and 3. I will especially focus on the combustion and the graphitisation of samples for radiocarbon dating and suggest some improvements for the graphitisation of small samples.

This study was meant to be published as a peer-reviewed article in an international journal. However, as our accelerator was put out of action, many questions were prevented from being answered completely, and some sections of this report might thus appear half-finished. The improvement of sample preparation for radiocarbon dating, especially the production of targets for the accelerator, was aimed at our unique combination of ion source and accelerator. Therefore, I could not compensate for our missing accelerator by sending targets to other laboratories (which I fortunately could do for many of the archaeological and geological samples). Regardless of the aforementioned shortcomings, this study still provides some results and considerations that should not be forgotten, as they might be a good basis for optimising the sample preparation for the new accelerator. The first preliminary results of this study can also be found in Philippersen (2008).

Many of the procedures in this study have been tested using two kinds of material. Standards are sample materials with known radiocarbon ages and δ$^{13}$C values. Backgrounds are $^{14}$C free samples for assessing the amount of modern contamination. Internally, samples are identified by sample IDs (SID), whereas AAR-numbers are used for reporting ages (see chapter 3). Different fractions of a sample are identified by sub-sample IDs (SSID). Every manipulation of a sub-sample (e.g. weighing, chemical treatment, combustion, graphitisation) results in a new SSID. The values belonging to the sub-samples as well as their precursors and successors are saved in a database (Kjeldsen et al., 2010).

4.1 CO$_2$ collection

The usual procedure for combustion and graphitisation of samples is presented in figure 2.4 in chapter 2. The proposed improvement of this method includes CO$_2$ collection for graphitisation after combustion in the elemental analyzer (Figure 4.1). This would save time and sample material (only weigh out one sample) as well as money (no need for quartz tubes and CuO), although potential extra costs for the trapping have to be taken into account. At the Aarhus AMS $^{14}$C Dating Centre, there are plans for automation of the graphitisation, and in this context, a CO$_2$-collection system would be especially useful: the whole process from combustion to graphitisation could be automated. In contrast, the samples would still have to be transferred manually into the automated graphitisation system when samples are com-
busted in quartz tubes.

It is therefore suggested to split the gas from combustion at the EA, let part of it enter the mass spectrometer for isotope ratio measurements, and collect CO$_2$ for radiocarbon dating from the rest of the gas.

An automatic gas handling system for collecting CO$_2$ from the elemental analyzer has already been developed by Jesper Olsen (Olsen et al., 2007). It is a cryogenic trapping device added in such a way that it is possible to shift between dual inlet isotope ratio measurement applications and the collection of CO$_2$ for AMS. Olsen et al. (2007) report a trapping efficiency of 38% to 84% when the system is running automatically, but 97% when dewar and needle are moved by hand. $\delta^{13}$C and $\delta^{15}$N values are measured from part of the gas, while CO$_2$ is collected from the majority of the gas. The $\delta^{13}$C and $\delta^{15}$N values measured during CO$_2$ collection agree with those from normal measurements. The $\delta^{13}$C values of the collected CO$_2$ agree as well, indicating that the splitting of the gas does not introduce fractionation (Olsen et al., 2007).

In routine operation, CO$_2$ gas from samples that have been combusted or acidified elsewhere is transported in manifold vials to the mass spectrometer for $^{13}$C and $^{18}$O measurements. A Gilson 220XL sampling robot transfers the CO$_2$ from the vials to the mass spectrometer. This system is shown in figure 4.2. In the case of CO$_2$ collection, the same Gilson robot is used the other way round for collecting the samples that were combusted in the EA and transferring the CO$_2$ into manifold vials to transport it to the graphitisation system.

However, this system had a disadvantage. It was not possible to know how much CO$_2$ had been collected. It would therefore be difficult to prepare the graphitisation of these samples (the catalyst has to be preconditioned, see section 2.1.2). It would not be possible to know in advance how many successfully trapped samples had to be graphitised, and whether big or small reactors would be required. When the sample size was known in advance, it would furthermore not be necessary to measure the amount of CO$_2$ in a calibrated volume on the graphitisation system, so one step of freezing–unfreezing could be left out.

Therefore, an extra device had to be developed for trapping the CO$_2$ and measuring its amount before collecting the CO$_2$ in the vials in which it is transferred to the graphitisation system. The known sample size will be an advantage for graphitisng the sample, as the required reactor size and amount of H$_2$ are known before the sample is transferred to the graphitisation system.

### 4.1.1 CO$_2$ trap experiments in Aarhus

Pneumatic valves, controlled by a computer that also controls the mass spectrometer, are used for realising this trapping system (figure 4.3). The four-port valve can switch between two positions. In the first one, the gas from the EA passes through the trap. In the second position, the trap is isolated so that gas coming from the EA is directly led to vent. For the trap we use a small copper tank that can be filled with liquid nitrogen using a pressure air pump. The actual trap is a stainless steel tube that is wrapped around this tank. For heating the trap after trapping, a heating wire is also wrapped around the copper tank. The trapped CO$_2$ is cryogenically transferred to sample vials.

The trapping is carried out as follows: The trap is cooled by filling the copper tank with liquid nitrogen. 99% of the CO$_2$ from the combustion are led through the trap by a constant flow of helium. The CO$_2$ freezes on the walls of the stainless steel tube. Then, helium and other gases that may be present in the trap are pumped away, the trap is sealed and warmed up again. The CO$_2$ is now again gaseous and once this closed volume is calibrated, the pressure measured here indicates the sample size.

When the pressure has been measured, the CO$_2$ is cryogenically transferred to one of the sample vials in the manifold bed (see figure 4.3). All the vials that we need for one batch of trapped samples are standing in a container filled with liquid nitrogen, and a robot arm moves the tube and needle through which the sample will be transferred to the respective vial (cf. Figure 4.2).

It is much easier to freeze pure CO$_2$ from a closed volume than trapping CO$_2$ cryogenically when it passes by in a stream of other gases. Therefore, some efforts have been put into developing and testing different trap designs. A similar situation is the preparation of water samples. There, the CO$_2$ from the water is transported in a stream of nitrogen gas (see chapter 3). One of the cryogenic traps from the water system is displayed in figure 4.4. Three cryogenic traps after one another are necessary for trapping all the CO$_2$. Therefore, three dewars with liquid nitrogen have to be put under the cryogenic traps. This is feasible for a few water samples, but would be too laborious for routine preparation of all sample types, and very complicated to automate. Therefore, some alternative trap designs have been tested during another series of experiments (see section 4.1.2).

As the objective is to trap samples for $^{14}$C dating, the fractionation and contamination introduced during the trapping procedure have to be estimated.
4.1. CO$_2$ COLLECTION

Figure 4.1: From chemically pretreated sample to $\delta^{13}$C, $\delta^{15}$N and $^{14}$C results - the proposed method with collection of CO$_2$ for graphitisation after combustion in the elemental analyzer. This method is suggested for samples where both radiocarbon dating, $\delta^{13}$C and $\delta^{15}$N measurement are requested, e.g. human bones or food crusts on pottery.

Figure 4.2: Sample transfer for $\delta^{13}$C and $^{18}$O dual inlet (DI) measurements. Left: The manifold bed and the Gilson 220 XL sampling robot. Right: Sample transfer from a manifold through a needle to the mass spectrometer.
CHAPTER 4. IMPROVEMENTS OF SAMPLE PREPARATION TECHNIQUES

Figure 4.3: Trapping CO₂ from EA combustion for graphitisation.

Figure 4.4: The preparation of water samples (DIC extraction) as an example for CO₂ trapping from a continuous flow of gases.
The fractionation can be examined by combustion and trapping of isotopic standards. In this case, the internal laboratory standards gelatine Gel A or Anthracite are used. The difference in δ¹⁴C between the obtained graphite and the original material indicates the extent of fractionation. This fractionation has to be compared with the fractionation that is introduced during the “traditional” sample combustion in quartz tubes.

Contamination is divided into two categories: modern, i.e. ¹⁴C containing, and old, i.e. ¹⁴C free. The extent of modern contamination is assessed by the preparation of ¹⁴C-free samples. If those background samples have a ¹⁴C age comparable to that of other background samples prepared with other methods, then the trapping procedure is suitable for routine preparation of old samples.

The samples were filled into tin capsules and combusted at the EA. The sample size in mg C is calculated from the sample size and the carbon content of the respective sample type: 90% for the background material Anthracite charcoal and 46% for the stable isotope working standard Gel A. The trapped amount of CO₂ was determined by cryogenically transferring the trapped CO₂ from the samples vials to a calibrated volume where the pressure of the CO₂ was measured.

The results of the trap tests are presented in table 4.1. The trapping efficiency is quite low. The installation of the new valves with lower leak rates resulted in better trapping efficiency. Still, 63% on average is too low, and the inconsistency of the yield is problematic. As shown in figure 4.3, 90% of the CO₂ from a sample should pass through the trap. One reason for the low trapping efficiency could be that some CO₂ passes the trap without being frozen. It is also possible that frozen CO₂ blocks the trap, not allowing the rest of the sample’s CO₂ to enter the trap. However, the trapping efficiency between 31% and 97% is comparable to the CO₂ collection efficiency reported by Olsen et al. (2007), 38% to 84% in automatic mode. The low efficiency in automatic mode was a result of problems with the CO₂ collection device; a needle was frequently blocked by rubber from the vial rubber septum. The result is thus not satisfactory, but promising, considering that I had added an extra step to the automatic CO₂ collection. However, in my case, the reason for the variability of the yield is not known.

To test how large a fractionation the low trapping efficiency results in, we graphitised the Gel A samples that were trapped with the new design. Then we measured the δ¹³C values of the graphite-catalyst mixture. Table 4.1 shows the results of these measurements. It can be seen that the fractionation is acceptable for sample preparation and not larger than for the usual combustion in quartz tubes (cf. figure 4.20).

The three last samples in table 4.1, background Anthracite, were graphitised and mounted in cathodes, as the contamination with modern carbon should be determined. However, these backgrounds were stored for a long time while I waited for the accelerator to be ready again, so I decided to discard them. Because of the long storage time, these samples would probably have accumulated modern contamination that would have masked any contribution from the trapping procedure. Fortunately, some samples from a later series of trapping experiments could be dated (Table 4.2).

One can preliminarily conclude that the trapped CO₂ is a good representation of the sample’s carbon, although the trapping efficiency might be low. As the trapping takes place while another fraction of gas from the same combustion is measured in the mass spectrometer, we also have to check these measurements. Table 4.2 shows the results of these measurements. Oxalic acid (C₆H₅O₄) and anthracite coal have no δ¹⁵N values as they do not contain nitrogen. Isotope ratios of the standards are given in table 4.5.

The samples were combusted and trapped in the order they appear in the table. The stable isotope values for the trapped gas and for the gas that was measured directly during the trapping process agree with the standard values (see table 4.5). Six of the trapped samples were ¹⁴C dated. The results (¹⁴C ages) of the three oxalic acid II samples and the three background anthracite samples are given in table 4.2.

The ¹⁴C ages determined during routine measurements are ca. 2300 ¹⁴C years BP for oxalic acid II and ca. 46,000 ¹⁴C years BP for background anthracite, so the trapped samples agree with the expected values. Apparently, the background values are better for the samples that were combusted after another background, which indicates a memory effect. Possible arrangements to eliminate this memory effect are, for example, warming the trap to higher temperatures between each sample, or flushing the system with He for a longer time between samples.

Although the results of stable isotope and ¹⁴C measurements of the trapped samples are promising, the inconsistent trapping efficiency is a serious problem, especially for very small samples. Experiments with different trap designs (see below) are needed to make trapping more efficient. A longer steel tube and longer trapping time could prevent CO₂ leaving the trap “untrapped”. A larger diameter of the tube could prevent blocking by frozen CO₂. The first attempt is more promising, because if there is a risk of blocking, it would be greater for larger samples. In ta-
Table 4.1: CO$_2$ trapping tests. The first nine tests were done with valves that had a higher leak rate than acceptable for the required vacuum range. New valves were installed and the volume of the tubes and fittings was reduced before the remaining trap tests. The trapped CO$_2$ from five of these samples was graphitised in big or small reactors (see below), and the $\delta^{13}$C values of the graphite were measured. The standard value for Gel A is $\delta^{13}$C = -21.81 permil.

<table>
<thead>
<tr>
<th>Sample material</th>
<th>Sample size (mg)</th>
<th>Sample size (mgC)</th>
<th>Trapped (mgC)</th>
<th>Trapping efficiency</th>
<th>reactor type</th>
<th>$\delta^{13}$C (%) VPDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>0.23</td>
<td>0.21</td>
<td>0.20</td>
<td>95%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>0.39</td>
<td>0.35</td>
<td>0.30</td>
<td>86%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>0.80</td>
<td>0.72</td>
<td>0.50</td>
<td>69%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>1.34</td>
<td>1.21</td>
<td>0.63</td>
<td>52%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>2.40</td>
<td>1.10</td>
<td>0.36</td>
<td>35%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>2.70</td>
<td>1.24</td>
<td>0.28</td>
<td>23%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>1.41</td>
<td>0.65</td>
<td>0.16</td>
<td>25%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>2.07</td>
<td>0.95</td>
<td>0.15</td>
<td>16%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>0.86</td>
<td>0.40</td>
<td>0.09</td>
<td>23%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>—</strong></td>
<td><strong>—</strong></td>
<td><strong>—</strong></td>
<td><strong>47%</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Replacement of valves</th>
<th>Sample size (mg)</th>
<th>Sample size (mgC)</th>
<th>Trapped (mgC)</th>
<th>Trapping efficiency</th>
<th>reactor type</th>
<th>$\delta^{13}$C (%) VPDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>0.49</td>
<td>0.44</td>
<td>0.28</td>
<td>64%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>1.04</td>
<td>0.94</td>
<td>0.29</td>
<td>31%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>1.12</td>
<td>0.52</td>
<td>0.45</td>
<td>87%</td>
<td>big</td>
<td>-23.11±0.10</td>
</tr>
<tr>
<td>Anthracite</td>
<td>0.49</td>
<td>0.44</td>
<td>0.28</td>
<td>64%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>1.04</td>
<td>0.94</td>
<td>0.29</td>
<td>31%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>1.12</td>
<td>0.52</td>
<td>0.45</td>
<td>87%</td>
<td>big</td>
<td>-23.18±0.10</td>
</tr>
<tr>
<td>Gel A</td>
<td>1.02</td>
<td>0.47</td>
<td>0.23</td>
<td>49%</td>
<td>big</td>
<td>-22.82±0.10</td>
</tr>
<tr>
<td>Gel A</td>
<td>0.75</td>
<td>0.35</td>
<td>0.19</td>
<td>54%</td>
<td>small</td>
<td>-21.62±0.10</td>
</tr>
<tr>
<td>Gel A</td>
<td>0.41</td>
<td>0.19</td>
<td>0.08</td>
<td>42%</td>
<td>small</td>
<td>-22.91±0.10</td>
</tr>
<tr>
<td>Gel A</td>
<td>1.02</td>
<td>0.47</td>
<td>0.27</td>
<td>57%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>0.86</td>
<td>0.40</td>
<td>0.27</td>
<td>68%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>2.26</td>
<td>1.04</td>
<td>0.68</td>
<td>65%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>1.93</td>
<td>0.89</td>
<td>0.41</td>
<td>46%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gel A</td>
<td>2.06</td>
<td>0.95</td>
<td>0.50</td>
<td>62%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>2.06</td>
<td>0.38</td>
<td>0.50</td>
<td>94%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>2.06</td>
<td>0.90</td>
<td>0.50</td>
<td>97%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>2.06</td>
<td>0.17</td>
<td>0.50</td>
<td>75%</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>—</strong></td>
<td><strong>—</strong></td>
<td><strong>—</strong></td>
<td><strong>63%</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: CO$_2$ trapping tests. The first nine tests were done with valves that had a higher leak rate than acceptable for the required vacuum range. New valves were installed and the volume of the tubes and fittings was reduced before the remaining trap tests. The trapped CO$_2$ from five of these samples was graphitised in big or small reactors (see below), and the $\delta^{13}$C values of the graphite were measured. The standard value for Gel A is $\delta^{13}$C = -21.81 permil.

ble 4.1, the trapping efficiency would thus be lower for larger samples, but such a tendency is not observed. The combustion in the EA might furthermore be incomplete – the samples for trapping are much larger than the samples we usually combust for stable isotope measurements. We use already larger amounts of oxygen for the combustion of samples for trapping, but more adjustments might be necessary. In addition, the amount of contamination with dead carbon should be measured by combusting and trapping oxalic acid samples of different sizes.

4.1.2 CO$_2$ trap experiments in Belfast

I had the opportunity to test some manual trapping devices with the EA at the $^{14}$CHRONO Centre, Queen’s University Belfast, to experiment with different designs. The reliability of $\delta^{13}$C values and $^{14}$C ages of the trapped CO$_2$ had been demonstrated before (see above). Therefore, stable isotope measurements and $^{14}$C datings were left out during these experiments.

The tested designs included different cryogenic traps (Figure 4.6) and a trap made of zeolite, a microporous aluminosilicate mineral. The first cryogenic trap made of glass was only used for very few experiments. Soon it became clear that the connections be-
4.1. CO₂ COLLECTION

<table>
<thead>
<tr>
<th>Material</th>
<th>SSID</th>
<th>Sample size [mg]</th>
<th>δ¹³C (%) VPDB</th>
<th>Δδ¹³C (%)</th>
<th>δ¹⁵N (%) AIR</th>
<th>Δδ¹⁵N (%)</th>
<th>¹³C age (uncal BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel A</td>
<td>34236</td>
<td>1.1</td>
<td>-21.85</td>
<td>-0.04</td>
<td>5.14</td>
<td>0.26</td>
<td>—</td>
</tr>
<tr>
<td>Gel A</td>
<td>34237</td>
<td>1.589</td>
<td>-21.76</td>
<td>0.05</td>
<td>5.74</td>
<td>0.34</td>
<td>—</td>
</tr>
<tr>
<td>Gel A</td>
<td>34238</td>
<td>3.33</td>
<td>-21.82</td>
<td>-0.01</td>
<td>5.32</td>
<td>-0.08</td>
<td>—</td>
</tr>
<tr>
<td>OX II</td>
<td>34241</td>
<td>4.62</td>
<td>-17.09</td>
<td>0.71</td>
<td>—</td>
<td>—</td>
<td>-2282±26</td>
</tr>
<tr>
<td>OX II</td>
<td>34242</td>
<td>4.787</td>
<td>-17.08</td>
<td>0.72</td>
<td>—</td>
<td>—</td>
<td>-2278±27</td>
</tr>
<tr>
<td>OX II</td>
<td>34243</td>
<td>2.078</td>
<td>-17.48</td>
<td>0.32</td>
<td>—</td>
<td>—</td>
<td>-2260±130</td>
</tr>
<tr>
<td>Bgd Anthracite</td>
<td>34244</td>
<td>0.88</td>
<td>-22.36</td>
<td>0.48</td>
<td>—</td>
<td>—</td>
<td>40900±1200</td>
</tr>
<tr>
<td>Bgd Anthracite</td>
<td>34245</td>
<td>0.641</td>
<td>-22.55</td>
<td>0.29</td>
<td>—</td>
<td>—</td>
<td>43000±2300</td>
</tr>
<tr>
<td>Bgd Anthracite</td>
<td>34246</td>
<td>1.165</td>
<td>-22.42</td>
<td>0.42</td>
<td>—</td>
<td>—</td>
<td>44800±1500</td>
</tr>
<tr>
<td>Bgd Anthracite</td>
<td>34247</td>
<td>0.501</td>
<td>-22.72</td>
<td>0.12</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Bgd Anthracite</td>
<td>34248</td>
<td>1.561</td>
<td>-22.45</td>
<td>0.39</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>34249</td>
<td>8.799</td>
<td>-1.13</td>
<td>2.71</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4.2: Stable isotope measurements of samples whose CO₂ was trapped at the same time. In six cases, the trapped CO₂ was radiocarbon dated.

During trapping, there is a continuous gas flow through the traps. The flow consists of Helium, the carrier gas from the EA, carrying the CO₂ and N₂ from sample combustion. The continuous He flow prevents air from entering the trap. Table 4.3 gives the results of the trapping experiments in Belfast. Figure 4.8 is a graphical representation of the trapping efficiency from table 4.3.

The cryogenic traps were filled with copper or quartz chippings in order to offer a large cold surface on which the CO₂ could freeze. For improving the trapping yield, the trap could be filled up with more quartz, which would increase the effective cold surface, but would slow down the gas flow. A possible problem with a too slow gas flow is that air might take the opposite direction and come into the trap from the atmosphere, but this can be tested with a blank: combusting and trapping a sample that does not contain carbon, e.g. an empty tin capsule, indicates how much atmospheric CO₂ enters the system. The combustion, trapping and dating of a radiocarbon-free sample indicates how much modern contamination enters the trap. One combustion blank, an empty tin capsule, was combusted. As no CO₂ was trapped, we can be confident that no significant air leaks were present in the system, and that the gas flow was sufficient to keep atmospheric CO₂ out of the trap.

As the trap was filled with copper during the first experiments, it was suspected that the following reaction could take place: CO₂ + 2Cu ⇌ 2CuO + C. The trap was therefore rebuilt using quartz chippings instead of copper. A11 is the first sample that was collected after the rebuilding under optimum conditions. While trapping A10, the liquid nitrogen supply was not sufficient. As the CO₂ collection had been unsatisfactory for the first many samples, it was suspected that there was a problem with the test material anthracite - e.g. incomplete combustion. For further tests, another material was used: Nicotinamide, which was known to combust well in the EA. The metal trap was later replaced by a new design of a glass trap (see table 4.3) which had been designed in cooperation with George Burton, glassblower at Queen’s University. There, the transition from big diameter in the trap to small diameter, as for the tubes from the EA, was mainly built in glass, so fewer potentially leaking connectors were needed.

The trapping efficiency of the cryogenic traps, i.e. the percentage of carbon from the sample that could be trapped, is plotted against the trapping time in figure 4.9. The trapping time is defined as the time from the end of sample combustion until the trapping procedure is ended by closing the trap valves. Furthermore, figure 4.9 displays the trapping percentage for all trap designs as a function of sample size.
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Figure 4.6: Manual cryogenic trapping devices. While trapping, the glass tube (left) / the U-shaped steel tube (right) is immersed in liquid nitrogen.
Table 4.3: CO\textsubscript{2} trap tests in Belfast: manual trapping devices

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>A1</td>
<td>614</td>
<td>≈200</td>
<td>95%</td>
<td>≈30%</td>
<td>metal trap</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A2</td>
<td>234</td>
<td>lost</td>
<td>95%</td>
<td></td>
<td>glass trap</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A3</td>
<td>260</td>
<td>9</td>
<td>95%</td>
<td>3.5%</td>
<td>glass trap</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A4</td>
<td>119</td>
<td>lost</td>
<td>95%</td>
<td></td>
<td>glass trap</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A5</td>
<td>195</td>
<td>46</td>
<td>95%</td>
<td>24%</td>
<td>25% of expected yield; 123/144 not frozen</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A6</td>
<td>8</td>
<td>103</td>
<td>95%</td>
<td>18%</td>
<td>19% of expected yield; 123/144 not frozen</td>
<td></td>
</tr>
<tr>
<td>Anthracite</td>
<td>A7</td>
<td>9</td>
<td>754</td>
<td>240</td>
<td>95%</td>
<td>32%</td>
<td>33% of expected yield; 130/156 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>A8</td>
<td>17</td>
<td>90</td>
<td>30</td>
<td>95%</td>
<td>34%</td>
<td>36% of expected yield; 135/157 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>A9</td>
<td>10</td>
<td>88</td>
<td>29</td>
<td>95%</td>
<td>32%</td>
<td>34% of expected yield; 101/118 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>A10</td>
<td>10</td>
<td>202</td>
<td>55</td>
<td>95%</td>
<td>27%</td>
<td>29% of expected yield; 114/132 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>A11</td>
<td>13</td>
<td>132</td>
<td>43</td>
<td>95%</td>
<td>32%</td>
<td>34% of expected yield; 120/139 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>A12</td>
<td>15</td>
<td>155</td>
<td>57</td>
<td>95%</td>
<td>37%</td>
<td>39% of expected yield; 104/123 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B1</td>
<td>16</td>
<td>209</td>
<td>100</td>
<td>95%</td>
<td>48%</td>
<td>50% of expected yield; 79/94 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B2</td>
<td>16</td>
<td>107</td>
<td>24</td>
<td>95%</td>
<td>22%</td>
<td>23% of expected yield; 165/193 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B3</td>
<td>16</td>
<td>87</td>
<td>19</td>
<td>95%</td>
<td>22%</td>
<td>23% of expected yield; 132/155 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B4</td>
<td>16</td>
<td>93</td>
<td>29</td>
<td>95%</td>
<td>31%</td>
<td>32% of expected yield; 128/151 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B5</td>
<td>15</td>
<td>735</td>
<td>350</td>
<td>95%</td>
<td>48%</td>
<td>50% of expected yield; 121/147 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B6</td>
<td>15</td>
<td>393</td>
<td>45</td>
<td>95%</td>
<td>12%</td>
<td>12% of expected yield; 171/176 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>B7</td>
<td>15</td>
<td>1485</td>
<td>595</td>
<td>95%</td>
<td>28%</td>
<td>30% of expected yield; 140/162 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B9</td>
<td>20</td>
<td>470</td>
<td>105</td>
<td>95%</td>
<td>22%</td>
<td>23% of expected yield; 173/203 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C3+4</td>
<td>25</td>
<td>1210</td>
<td>229</td>
<td>95%</td>
<td>19%</td>
<td>32% of expected yield; 146/172 not frozen</td>
</tr>
<tr>
<td>Anthracite</td>
<td>B8</td>
<td>15</td>
<td>1387</td>
<td>683</td>
<td>95%</td>
<td>40%</td>
<td>52% of expected yield; 89/111 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C2</td>
<td>15</td>
<td>1485</td>
<td>595</td>
<td>95%</td>
<td>40%</td>
<td>68% of expected yield; 90/113 not frozen</td>
</tr>
<tr>
<td>blank</td>
<td>B12</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>77/88 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C5</td>
<td>15</td>
<td>561</td>
<td>160</td>
<td>95%</td>
<td>28%</td>
<td>48% of expected yield; 76/89 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C6</td>
<td>15</td>
<td>554</td>
<td>226</td>
<td>95%</td>
<td>41%</td>
<td>69% of expected yield; 77/91 not frozen</td>
</tr>
</tbody>
</table>
## Table 4.3: CO$_2$ trap tests in Belfast: manual trapping devices

<table>
<thead>
<tr>
<th></th>
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<td>Nicotinamide</td>
<td>C7</td>
<td>16</td>
<td>553</td>
<td>202</td>
<td>50%</td>
<td>37%</td>
<td>62% of expected yield; 66/79 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C8</td>
<td>17</td>
<td>524</td>
<td>238</td>
<td>50%</td>
<td>45%</td>
<td>77% of expected yield; 59/70 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C9</td>
<td>16</td>
<td>535</td>
<td>164</td>
<td>50%</td>
<td>31%</td>
<td>52% of expected yield; 66/78 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C10</td>
<td>17</td>
<td>488</td>
<td>114</td>
<td>50%</td>
<td>23%</td>
<td>40% of expected yield; 69/80 not frozen</td>
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<tr>
<td>new glass trap</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C11</td>
<td>16</td>
<td>490</td>
<td>33</td>
<td>50%</td>
<td>7%</td>
<td>12% of expected yield; 187/188 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>C12</td>
<td>17</td>
<td>730</td>
<td>105</td>
<td>50%</td>
<td>14%</td>
<td>24% of expected yield; 191/219 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D1</td>
<td>15</td>
<td>524</td>
<td>98</td>
<td>50%</td>
<td>19%</td>
<td>32% of expected yield; 184/211 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D2</td>
<td>6</td>
<td>450</td>
<td>55</td>
<td>50%</td>
<td>12%</td>
<td>21% of expected yield; 168/190 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D3</td>
<td>15</td>
<td>460</td>
<td>83</td>
<td>50%</td>
<td>18%</td>
<td>31% of expected yield; 164/185 not frozen</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D4</td>
<td>3</td>
<td>462</td>
<td>62</td>
<td>50%</td>
<td>13%</td>
<td>23% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D5</td>
<td>1</td>
<td>422</td>
<td>40</td>
<td>50%</td>
<td>10%</td>
<td>16% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D6</td>
<td>7</td>
<td>263</td>
<td>50</td>
<td>50%</td>
<td>19%</td>
<td>32% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D7</td>
<td>5</td>
<td>1224</td>
<td>143</td>
<td>50%</td>
<td>12%</td>
<td>20% of expected yield</td>
</tr>
<tr>
<td>zeolite trap</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D8</td>
<td>6</td>
<td>446</td>
<td>307</td>
<td>50%</td>
<td>69%</td>
<td>117% of expected yield</td>
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<tr>
<td>Nicotinamide</td>
<td>D9</td>
<td>5</td>
<td>414</td>
<td>212</td>
<td>50%</td>
<td>51%</td>
<td>87% of expected yield</td>
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<tr>
<td>Nicotinamide</td>
<td>D10</td>
<td>8</td>
<td>627</td>
<td>69</td>
<td>50%</td>
<td>11%</td>
<td>19% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>D11</td>
<td>4</td>
<td>524</td>
<td>198</td>
<td>50%</td>
<td>38%</td>
<td>64% of expected yield</td>
</tr>
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<td>Nicotinamide</td>
<td>D12</td>
<td>4.5</td>
<td>472</td>
<td>86</td>
<td>50%</td>
<td>18%</td>
<td>31% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E1</td>
<td>3.5</td>
<td>501</td>
<td>221</td>
<td>50%</td>
<td>44%</td>
<td>75% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E2</td>
<td>3</td>
<td>441</td>
<td>0</td>
<td>50%</td>
<td>0%</td>
<td>0% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E3</td>
<td>4</td>
<td>579</td>
<td>155</td>
<td>50%</td>
<td>27%</td>
<td>45% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E4</td>
<td>3.75</td>
<td>448</td>
<td>183</td>
<td>50%</td>
<td>41%</td>
<td>69% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E5</td>
<td>3.5</td>
<td>433</td>
<td>114</td>
<td>50%</td>
<td>25%</td>
<td>43% of expected yield</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E11</td>
<td>5</td>
<td>491</td>
<td>33</td>
<td>50%</td>
<td>7%</td>
<td>12% of expected yield; cleaned prior to trapping</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>E12</td>
<td>4.5</td>
<td>467</td>
<td>57</td>
<td>50%</td>
<td>12%</td>
<td>21% of expected yield; cleaned prior to trapping</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>F1</td>
<td>4</td>
<td>596</td>
<td>314</td>
<td>50%</td>
<td>53%</td>
<td>89% of expected yield; cleaned prior to trapping</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>F2</td>
<td>3.5</td>
<td>545</td>
<td>74</td>
<td>50%</td>
<td>14%</td>
<td>23% of expected yield; cleaned prior to trapping</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>F3</td>
<td>4.25</td>
<td>567</td>
<td>129</td>
<td>50%</td>
<td>23%</td>
<td>38% of expected yield; cleaned prior to trapping</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>F4</td>
<td>3.75</td>
<td>471</td>
<td>105</td>
<td>50%</td>
<td>22%</td>
<td>38% of expected yield; cleaned prior to trapping</td>
</tr>
</tbody>
</table>
4.1. CO₂ COLLECTION

Figure 4.7: Cooling of the zeolite trap. Blue diamonds: passive cooling. Pink squares: active cooling.

For cryogenic trapping, a trap time of 10 minutes was assumed to be sufficient. Usually, after 10 minutes, all sample and reference gas peaks have passed through the system (the delay is a result of the GC column which is needed for separating CO₂ and N₂). To test the influence of the trapping time, two samples of almost equal size were combusted under the same circumstances and trapped for 17 minutes (A8) and 10 minutes (A9). There is no significant difference in measured trapped carbon yield (table 4.3). In conclusion, the cryogenic traps are not reliable enough. Experiments with different combination of valves and tubes indicated that some CO₂ might already freeze before it enters the actual trap. Especially the transition from thin to thick tubes seems to be problematic.

The zeolite trap absorbs CO₂ at room temperature and releases it at ca. 500°C. The zeolite trap is equipped with two pairs of inlet and outlet, for the gas flow and for pressurized air for cooling the trap, respectively. Furthermore, a heating wire is connected with the trap. The pressurized air may cool the trap rapidly, but trapping also works without cooling. It is feasible just to wait until the trap has cooled down. Alternatively, blowing cool air into the pressurized-air inlet with a hair dryer (set on cool, obviously) can accelerate the cooling substantially. Figure 4.7 displays the cooling of the zeolite trap after it had been heated to 500°C. It takes almost an hour for the trap to cool down to the suggested trapping temperature of ca. 30°C. Active cooling can reduce this time to about 15 minutes.

Figure 4.10 plots the yields from the zeolite trap against trapping time. The yields were very variable. However, this changed when a cleaning procedure, 5 minutes at 500°C while being flushed with Helium immediately prior to trapping, was implemented (Figure 4.10). Apparently, the yield depends strongly on the trapping time. For these experiments with the zeolite trap, the trapping time was measured as the time from the beginning of the sample combustion to the closing of the trap valves. It was easier to determine the start time for combustion, as this was indicated by EA valves opening/closing, than the end time for combustion, as the end of the combustion was identified visually.

The trap valves had to be operated manually. Therefore, it was difficult to obtain highly precise trapping times. For future studies, the trap valves should be operated electronically by the same computer that operates the EA, so combustion and trapping can be adapted to each other. If the high yield of the zeolite trap at a certain trapping time can be confirmed, measurements of the trapped CO₂ will indicate the reliability of this trap. Especially the risk of memory effects should be examined by alternately trapping background and modern samples, and radiocarbon dating them.

If both cryogenic and zeolite trap gave the same results, zeolite traps would be preferable for routine operation as they do not require liquid nitrogen, only connections for heating wire and pressurized air. Zeolite traps would thus be easier to integrate into laboratory routine.

The aim of the experiments in Belfast had been to test different possibilities for trapping CO₂. It was demonstrated that cryogenic traps do not work if there are large volumes into which the H₂-flow (transporting the CO₂) can spread. A final cryogenic trap design should thus work as much as possible with the 1/16” tubes, in which the H₂-CO₂-mixture is transferred from the EA. The transition to tubes with larger diameter should be avoided. A possible design could include two needles in a sealed glass tube.
CHAPTER 4. IMPROVEMENTS OF SAMPLE PREPARATION TECHNIQUES

Trapped % of sample’s carbon, in chronological order

Figure 4.8: Percentage of the carbon present in a sample that could be trapped with the respective trapping device during the experiments in Belfast. See table 4.3.

Figure 4.9: Trapped yield of traps tested in Belfast. Right: Yield against trapping time for cryogenic traps. Left: Yield against sample size for cryogenic and zeolite traps.

Figure 4.10: Trapped yield against trapping time for the zeolite trap. Right: without pre-cleaning. Left: after pre-cleaning (5 minutes at 500°C with He flow).
4.2 Combustion in quartz tubes

The aim of this study is to improve the preparation of small samples. The question is thus, do we have to adjust the combustion method for small samples, or can they be combusted in the same way as normal-sized samples without being affected by more fractionation?

Two blanks were combusted, i.e. quartz tubes with 200 mg CuO, but without sample. They yielded 0.01 and 0.02 mgC, respectively. These are small amounts compared with the usual sample size of 1 mgC, but compared to some small samples, 0.01 and 0.02 mgC are quite large amounts. Further tests with small background samples and standards are needed for quantifying the radiocarbon age of this contamination. The effects of a constant contamination can be corrected when combusting standards and back-ground samples and standards are needed for quantifying the radiocarbon age of this contamination. Unfortunately, our accelerator was put out of action before some of these samples could be measured.

Furthermore, Gel A was weighed out into three quartz tubes. The sizes were chosen in a way that one combustion yielded carbon for four graphitisations (quadruplet), one for two (doublet), and one for one graphitisation. Between 0.23 and 0.25mgC were graphitised in small reactors (big/small reactors will be presented below). The results are given in table 4.4. Standard $\delta^{13}C$ and pmC values for Gel A can be found in table 4.5.

The weighted mean of the four (quadruplet) or two (doublet) EA-CN $\delta^{13}C$-measurements is calculated by weighting the $\delta^{13}C$-values with the deviation of the measured CO$_2$ peak height $p.h.$ from the ideal CO$_2$ peak height of 10:

$$\delta^{13}C = \sum_{n} \frac{\delta^{13}C_n}{(10 - p.h.n)^2}$$

(4.1)

When the peak height is significantly lower or higher (“overrange”) than 10, the measurement becomes unreliable. In the case of SSID30749-51, all peak heights were high/low enough so no measurement had to be discarded. However, with weighting the measurements with how well they approach the ideal peak height, one makes sure that the most reliable measurements count most. The weighted means of the EA $\delta^{13}C$ measurements are displayed in table 4.4. In fact, a calibration curve should have been produced, for finding the relation between sample size (and thus peak height) and $\delta^{13}C$ values in order to correct the $\delta^{13}C$ values for effects of small sample size. However, this would have been too great an effort for the few samples I analysed here. Especially the incorporation of such corrections into our database would have cost too much time.

All $\delta^{13}C$-measurements, both DI, EA and the weighted means, are given in figure 4.11. The combustion does not result in significant fractionation, only about 0.2‰, and not systematically. An effect of sample size on the $\delta^{13}C$ value after combustion can thus not be found in these samples.

The effect of the combustion of different amounts of sample on the radiocarbon age were planned to be investigated. Slightly different amounts of the internal standard material Gel A were combusted in quartz tubes for graphitisation and $^{14}C$ measurement (table 4.6). The sample sizes of the graphite are more or less the same, so the effect of the different sizes in combustion will not be masked by a size effect of the graphitisation. Therefore, the normal combustion time of one hour can be applied to all following samples. A higher measured yield is the result of measurement uncertainties.

Furthermore, the CO$_2$ from these combustions was graphitised and the resulting graphite-catalyst mixture divided into sub-samples containing about 100 $\mu$g each. These were placed in tin cups and measured with the elemental analyser (EA) coupled to the mass spectrometer (see chapter 3 for a description of the measurement procedure, table 4.7 for the results). The $\delta^{13}C$ values which were measured on different sub-samples from the same graphitisation agree fairly well. This indicates that the reduced graphite is quite homogeneous, and that graphitisation and EA measurement do not introduce random fractionation.

In figure 4.12, the $\delta^{13}C$ values, averages of all $\delta^{13}C$ values measured for one combustion and graphitisation, are plotted as a function of combusted sample size ($\mu$g Gel A). Blue diamonds indicate one hour combustion, pink squares three hours. As the standard value for Gel A is -21.81‰, all measured values are too low. This fractionation is larger for smaller samples, in contrast to the results in table 4.4. Furthermore, three-hour combustion introduces larger fractionation than one-hour combustion.

However, size effects in the mass spectrometer
### Chapter 4. Improvements of Sample Preparation Techniques

#### Table 4.4: Combustion and graphitisation of different sample sizes of Gel A. The standard values for Gel A are 107.6 pmC and δ¹³C = -21.81‰. See figure 4.11 for a graphical representation of these measurements.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Material</th>
<th>pmC</th>
<th>δ¹³C</th>
<th>δ¹⁵N</th>
</tr>
</thead>
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<tr>
<td>bgl db sp</td>
<td>Iceland spar (calcite)</td>
<td>0</td>
<td>-3.84</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>Oxalic acid</td>
<td>103.979</td>
<td>-19.0</td>
<td>—</td>
</tr>
<tr>
<td>Ox-II</td>
<td>Oxalic acid</td>
<td>134.06</td>
<td>-17.8</td>
<td>—</td>
</tr>
<tr>
<td>bgl graphite</td>
<td>graphite</td>
<td>0</td>
<td>ca. -25.7</td>
<td>—</td>
</tr>
<tr>
<td>bgl anthracite</td>
<td>anthracite coal</td>
<td>0</td>
<td>-22.84</td>
<td>—</td>
</tr>
<tr>
<td>bgl gw</td>
<td>Background groundwater (dissolved Iceland spar)</td>
<td>0</td>
<td>ca. -3.84</td>
<td>—</td>
</tr>
<tr>
<td>Gel A</td>
<td>gelatine</td>
<td>107.6</td>
<td>-21.81</td>
<td>5.4</td>
</tr>
<tr>
<td>bgl wood</td>
<td>wood</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 4.5: Radiocarbon concentrations in percent modern carbon (pmC) and δ¹³C values, if known, of the standard materials used in this study.
4.2. COMBUSTION IN QUARTZ TUBES

Figure 4.11: $\delta^{13}$C measurements (DI on CO$_2$, EA on graphite) as well as the weighted means of the graphite $\delta^{13}$C measurements for Gel A subsamples no. 30749, 30750 and 30751 (Table 4.4).

Table 4.6: Combustion and $^{14}$C measurements of Gel A. An aliquot of the CO$_2$ from the combustion, corresponding to about 0.9-1.0 mgC, was used for graphitisation and $^{14}$C dating. The standard pmC value of Gel A is 107.6 (Table 4.5). The samples marked with — could not be measured because our accelerator was put out of action.

Could have changed $\delta^{13}$C values. In case the peak height in the mass spectrometer deviates strongly from the optimum, wrong $\delta^{13}$C values can be measured. To test this, the $\delta^{13}$C values which were averaged in figure 4.12, are displayed depending on the carbon fraction of the graphite-catalyst mixture in figure 4.13. It can be seen that the carbon fraction has a large effect on the $\delta^{13}$C values.

When correcting for the effect of carbon fraction (concentration of carbon in the sample for the mass spectrometer), the values from figure 4.12 display a less clear behaviour (Figure 4.14). Still, the fractionation effect is larger for samples that had been combusted for three hours, and slightly larger for the smallest sample sizes. Previous measurements had not resulted in a size dependency of the fractionation introduced by combustion (Table 4.4).

In conclusion, the fractionation, defined as the deviation of the measured values from the standard values of -21.81‰ for Gel A, is larger for the longer combustion time. It is therefore again recommended not to extend the combustion time. Furthermore, the average fractionation may be larger for smaller combusted sample sizes, although my results are ambiguous. This emphasizes the necessity of combusting small standards and backgrounds along with small samples.

The usual amount of 200-210 mg CuO, which is
1 hour combustion | 3 hours combustion
---|---
SSID | Mass (mg) | Yield (%) | δ\(^{13}\)C (EA) | SSID | Mass (mg) | Yield (%) | δ\(^{13}\)C (EA)
20655 | 0.33 | 47.7 | -28.28 | 20690 | 0.30 | 46.9 | -30.80
20722 | 0.390 | 50.1 | -30.73 | 20695 | 0.62 | 35.1 | -26.82
20718 | 0.606 | 39.2 | -30.75 | 20659 | 0.68 | 43.7 | -24.70
20722 | 0.390 | 50.1 | -30.73 | 20695 | 0.62 | 35.1 | -26.82
20664 | 0.87 | 43.4 | -24.33 | 20700 | 0.92 | 40.8 | -26.69
20669 | 1.16 | 43.6 | -24.25 | 20706 | 1.16 | 44.4 | -25.56
20674 | 1.49 | 38.0 | -23.69 | 20712 | 1.54 | 37.3 | -24.52
Average | 43.3±1.7 | -24.64 | Average | 40.9±2.2 | -26.26

Table 4.7: Combustion of Gel A, 1 hour compared to 3 hours. The averages were calculated without SSID-20684, 20718 and 20722, as these had been combusted with 100 mg CuO instead of the usual 200 mg.

Figure 4.12: δ\(^{13}\)C values of Gel A samples that were combusted in quartz tubes and graphitized, as a function of combusted sample size. Blue diamonds: one hour combustion. Pink squares: three hours combustion.

Figure 4.13: δ\(^{13}\)C values of Gel A samples as a function of carbon fraction.

A few tests have been performed where standards between ca. 200 and 700 μg were combusted with 100 mg CuO. The results are displayed in table 4.8. In all cases, the deviations from the standard values are huge. It is thus strongly recommended to use 200 mg CuO for combustion, even when the samples are small. The strange combustion yields for the graphite samples, 166 and 52%, can not be explained yet. The theoretical value is 100%.

used for combustion, corresponds to 2.51–2.64 mmol (CuO has 79.545 g/mol). One mole of carbon can be combusted with two moles of CuO (2 CuO + C → 2 Cu + CO\(_2\)). 200–210 mg CuO can thus be used for the combustion of 1.26–1.32 mmol pure carbon, which corresponds to 15–16 mgC. Real samples contain of course other elements than carbon which also have to be oxidised, but this estimate indicates already that the CuO amount is plenty for big samples. For small samples, the CuO amount could possibly be reduced.

Theoretical value is 100%.
4.3. GRAPHITISATION

<table>
<thead>
<tr>
<th>SSID</th>
<th>Mass (mg) and material</th>
<th>Yield (%)</th>
<th>δ(^{13})C (EA) (% VPDB)</th>
<th>deviation from std</th>
</tr>
</thead>
<tbody>
<tr>
<td>21902</td>
<td>0.20 graphite</td>
<td>166</td>
<td>-16.16</td>
<td>+9.57</td>
</tr>
<tr>
<td>20803</td>
<td>0.48 Gel A</td>
<td>44.3</td>
<td>-26.77</td>
<td>-4.96</td>
</tr>
<tr>
<td>20807</td>
<td>0.33 Gel A</td>
<td>52.4</td>
<td>-29.51</td>
<td>-7.70</td>
</tr>
<tr>
<td>21583</td>
<td>0.63 Ox-I</td>
<td>19.0</td>
<td>-26.92</td>
<td>-7.92</td>
</tr>
<tr>
<td>21587</td>
<td>0.23 graphite</td>
<td>52.0</td>
<td>-16.62</td>
<td>+9.11</td>
</tr>
<tr>
<td>21591</td>
<td>0.50 Gel A</td>
<td>34.6</td>
<td>-26.39</td>
<td>-4.58</td>
</tr>
<tr>
<td>21595</td>
<td>0.29 Gel A</td>
<td>41.3</td>
<td>-24.37</td>
<td>-2.56</td>
</tr>
<tr>
<td>21599</td>
<td>0.68 Ox-I</td>
<td>17.6</td>
<td>-16.10</td>
<td>+2.90</td>
</tr>
<tr>
<td>20718</td>
<td>0.606 Gel A</td>
<td>39.2</td>
<td>-30.75</td>
<td>+8.94</td>
</tr>
<tr>
<td>20722</td>
<td>0.390 Gel A</td>
<td>43.2</td>
<td>-26.86</td>
<td>+5.05</td>
</tr>
</tbody>
</table>

Table 4.8: Combustion of different amounts of standards with 100 mg CuO instead of 200 mg. The δ\(^{13}\)C values of the standard materials are given in table 4.5.

Figure 4.14: δ\(^{13}\)C values of Gel A samples that were combusted in quartz tubes and graphitised, as a function of combusted sample size. Corrected for mass spectrometer sample size effects as explained in the text. Blue diamonds: one hour combustion. Pink squares: three hours combustion.

4.3 Graphitisation

The principles of graphitisation are described in section 2.1.2. Here, I will present some attempts to improve the graphitisation, especially for small (<0.4 mgC) samples. A good graphitisation method is characterized by its rate (the reaction finishes after a reasonable amount of time) and reliability (no failed, delayed or incomplete reactions). The optimum procedure must be best in three categories, graphitisation characteristics, fractionation and cathode performance. If a constant fractionation occurs during sample preparation and measurement, this will not influence the radiocarbon dating, as samples, standards and backgrounds are processed with the same methods. However, fractionation always indicates an incomplete reaction, and is thus a measure of the quality of the method used, together with the consistency of the fractionation.

As mentioned in section 2.1.2, I will follow an empirical approach for optimising the graphitisation procedure. The effect of changes in e.g. reactor volume or catalyst material on reaction rate, isotopic fractionation and graphite characteristics is examined. The three catalyst types tested in this study are listed in table 4.9. With the manual graphitisation systems currently used in Aarhus, the reaction rate is less important as the graphitisation is prepared during the day and left to react overnight. However, a shorter reaction time minimizes the risk of contamination through air leaks (Smith et al., 2007), and could be an advantage with an automated graphitisation system.

The graphite produced must be easy to handle and compress to a target, and it must produce a high beam current during a sufficiently long lifetime in the AMS system. While these graphitisation experiments were performed, a new ion source was installed at our AMS system. It had been noted that the life time of cathodes in the new ion source was very low. Typically, the samples would only last for one-two runs (8 cycles per run). The total output was high enough, though, to produce higher precision dates than with the old ion source. The short life time made radiocarbon dating quite risky; there was for example not enough time to optimise settings for small samples before they were burnt out. Different strategies have been chosen for attempting to improve the life time of the cathodes:

- mix powder of metals or metal oxides with the graphite-catalyst while graphitising or mounting
it in the cathode
• use iron instead of cobalt as catalyst for graphitisation
• use different amounts of catalyst for graphitisation
• mount the cathodes in a different way, e.g. hammering in drilled cathodes

It had been planned to develop the graphitisation for small samples so far that it could be applied to my archaeological and geological samples in the other sub-projects, but different factors delayed the instrumental developments. The worst delay, the construction works in the basement, turned out to prevent the conclusion of the methodological study completely by destroying our accelerator. However, some of the improvements suggested here were applied to some of the small archaeological samples. Several were graphitised with iron instead of cobalt, and for the smallest archaeological samples, the small reactors tested here were used.

4.3.1 Graphitisation rate and completeness

Here, all graphitisation experiments are listed and pressure curves following the reactions are shown. The different catalysts used in these experiments are presented in table 4.9. Other parameters examined here are the amount of catalyst, or the graphite/catalyst ratio, and the graphitisation volume. The samples were graphitised either in the usual “normal-sized” reactors (in this context also called “big”, 4.5 cm$^3$) or in new small reactors (0.8 cm$^3$, only for samples up to 0.25 mgC, see figure 4.15), with iron or one of the cobalt types (Table 4.9). When the reactor size is reduced, the pressure increases and with it the collision rate of the gas molecules in the reactor. The effect of reduced reactor size for smaller samples has been used by other groups, e.g. Hua et al. (2001). The reaction volumes are denoted R followed by a number, the first digit indicating the graphitisation system (1 or 2), the other the reaction volume on that system (0–7 for system 2, where only big reactors are installed, and 0–11 for system 1, where in addition to eight normal-sized reactors, 4 new small reactors were installed). R10–R17 and R20–R27 are thus big, R18–R111 small reactors.

Figure 4.16 summarizes the graphitisation of different amounts of CO$_2$ in big or small reactors, with one of the three catalyst types. For all graphitisations pressure curves, only the first 5 hours are plotted. Not all graphitisations were finished at that time; many of them continued over night. Further information about the samples from the pressure curves can be found in the appendix, section A.

Effect of choice of catalyst

Figure 4.16 summarizes graphitisations with large and small reactors, Fe and Co catalysts and different sample sizes. Only the first 300 minutes of the reactions are plotted. This shows differences in the reaction rate, but not the effectivity of the reaction. Only graphitisations with iron are completed before 300 minutes.

It can be observed that graphitisation with iron is both faster and “more complete”, reaching a lower end pressure, than graphitisation with cobalt. Furthermore, for a given catalyst, the graphitisation of small samples in small reactors is faster than in big reactors (Figure 4.16). For two graphitisations, chromium was added to the catalyst (Goodfellow Chromium (Cr) Powder, LS27407 L O, CR006 020 /1, max. particle size 200 micron, purity 99.0%). The chromium has not changed the graphitisation characteristics (see figure 4.16, graphitisation of 0.900-0.999 mgC and 1.000-1.099 mgC). In addition to that, the following observations have been made, ordered after sample size:

For samples between 1.000 and 1.099 mgC, lower left in figure 4.16, the new Co starts the reaction as fast as Fe, but then the reaction slows down and the pressure curves for the new Co “meet” the pressure curves for the old Co and the pressure curves of the two Co types are from now on indistinguishable. The reactions with Fe are finished after less than three hours; the reactions with Co (old and new) take more than the plotted five hours.

0.900 to 0.999 mgC, lower right in figure 4.16: Most of the graphitisations with the new Co start faster than those with old Co, but become eventually slower. The reaction with iron proceeds as for the samples with 1.000–1.099 mgC.

0.500 to 0.699 mgC and 0.300 to 0.499 mgC, in the middle of figure 4.16: The graphitisations with Fe are already finished after 90 minutes. The reactions with old and new cobalt are as described for the bigger samples.

0.200 to 0.299 mgC, upper right in figure 4.16: Two graphitisations with Fe in big reactors are finished after 90 minutes. The one that is very slow is a water sample, and it has been observed before that the graphitisation of water samples is slower/harder to start. The graphitisations with old/new Co are almost indistinguishable. Graphitisations with Co in small reactors are (almost all) faster than those in big reactors.
4.3. GRAPHITISATION

<table>
<thead>
<tr>
<th>Name</th>
<th>Type, manufacturer etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old Cobalt</td>
<td>spherical Co powder, -325 mesh (&lt;45 microns), from Johnson Matthey GmbH Alfa Products, article no. 00739, manufacturing ceased</td>
</tr>
<tr>
<td>New Cobalt</td>
<td>cobalt powder, 2-4 micron 99+, 009093, Ch. 150799 MaTeck GmbH</td>
</tr>
<tr>
<td>Iron</td>
<td>iron reduced, grain size 10 micron, from Merck KGaA (article no. 3819)</td>
</tr>
</tbody>
</table>

Table 4.9: Catalysts used for the experiments

Figure 4.15: Normal-sized and small graphitisation reaction volumes (“reactors”). The peltier coolers are placed at the glass tube in which water is frozen. On top, a pressure transducer is installed. To the left, the green valve connects the reaction volume with the rest of the system.
0.100 to 0.199 mgC, upper left in figure 4.16: The fastest reaction is obtained with Fe in small reactors. The second-fastest is with Fe in big reactors, and the slowest, Co in big reactors. All graphitisations in small reactors reach a better “level of completeness” than those in big reactors. Graphitisations with Co in small reactors are in this regard superior to graphitisations with Fe in big reactors.

In conclusion, Fe is always recommended as catalyst for obtaining optimal graphitisation rates. For samples below 0.25 mgC, small reactors should be used for obtaining a satisfactory graphitisation. However, for making a final decision, graphite characteristics, fractionation and background levels must also be considered (see below).

Effect of amount of catalyst

Figure 4.17 displays the effect of different amounts of iron or cobalt, or of different catalyst ratios. The amounts of \( \text{CO}_2 \) for graphitisation (mgC) as well as the weight of catalysts (mg) and the graphite-to-catalyst ratios are noted on the figure. The amount of catalyst or graphite-to-catalyst ratio has no systematic influence on the reaction rate (e.g. how much the pressure decreases after the start of the reaction), or effectivity (i.e. how low the end pressure is). Therefore, the amount or ratio which proves to result in the best performance of the graphite-catalyst mixture during mounting and measurement should be chosen.

Table 4.10 summarizes the characteristics of the graphite-catalyst mixture under mounting into cathodes. Samples that were graphitised with iron tend to stick to the copper sheet which covers the graphite-catalyst mixture during pressing, instead of sticking to the aluminum cathode. Samples around 1 mgC were graphitised in big, samples with 0.2 mgC in small reactors. C-24466 is the only exception, a small sample graphitised in a big reactor. Unfortunately, most of these samples could not be measured. Only four samples that had been graphitised with cobalt were dated (see table 4.10). The amount of cobalt does not seem to influence the measurement, although four samples are not enough to show a clear tendency. Apparently, the added chromium had no effect, either.

A different method of mounting has also been tried (cf. the table in section A). This included predrilled holes in the cathodes, into which the graphite-catalyst mixture was filled. The sample was compressed by hammering, using a pin that could easily be cleaned between samples. This had an advantage over the method of pressing with copper sheets as the sample stuck to the cathode, and not to the copper sheet as happened often when mounting graphite-iron mixtures (see above). However, as a new pneumatic press is being developed for target preparation, and a different cathode design might be needed for the new ion source and accelerator, I will not dwell on different mounting methods.
4.3. GRAPHITISATION

Figure 4.16: Pressure curves for graphitisation of different amounts of CO₂.
<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>Pressure (fraction of start pressure)</th>
<th>Graphitation with different amounts of cobalt or iron. Bold numbers denote the graphite/catalyst ratio.</th>
<th>Time (Minutes)</th>
<th>Pressure (fraction of start pressure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1mgC 0.21mg Co R10: 4.76</td>
<td>1mgC 0.49mg Co R11: 2.04</td>
<td>0</td>
<td>1.11</td>
</tr>
<tr>
<td>5</td>
<td>1mgC 0.49mg Co R11: 2.04</td>
<td>0.2mgC 0.8mg Co R13: 0.25</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>1mgC 2.64mg Co R15: 0.38</td>
<td>1mgC 1.43mg Co R16: 0.70</td>
<td>10</td>
<td>0.9</td>
</tr>
<tr>
<td>20</td>
<td>1mgC 1.43mg Co R16: 0.70</td>
<td>1mgC 0.66mg Co+0.90mg Cr R17: 1.52</td>
<td>20</td>
<td>0.8</td>
</tr>
<tr>
<td>25</td>
<td>0.2mgC 0.39mg Co R18: 0.51</td>
<td>0.2mgC 1.38mg Co R19: 0.14</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>50</td>
<td>0.2mgC 1.38mg Co R19: 0.14</td>
<td></td>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td>0.1mgC 1.9mg Co+0.90mg Cr R17: 1.52</td>
<td></td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>200</td>
<td>0.1mgC 1.9mg Co+0.90mg Cr R17: 1.52</td>
<td></td>
<td>200</td>
<td>0.4</td>
</tr>
<tr>
<td>250</td>
<td>0.1mgC 1.9mg Co+0.90mg Cr R17: 1.52</td>
<td></td>
<td>250</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Figure 4.17: Graphitisations with different amounts of cobalt or iron. Bold numbers denote the graphite/catalyst ratio.
### 4.3. GRAPHITISATION

<table>
<thead>
<tr>
<th>C-no.</th>
<th>amount (mg) &amp; type of catalyst</th>
<th>mgC</th>
<th>sample material</th>
<th>appearance, mounting characteristics, pmC</th>
</tr>
</thead>
<tbody>
<tr>
<td>24464</td>
<td>0.21 Co</td>
<td>1.04</td>
<td>bgd dbsp</td>
<td>fell out, mounted again, silver visible in surface pmC 0.83±0.03</td>
</tr>
<tr>
<td>24465</td>
<td>0.49 Co</td>
<td>0.97</td>
<td>bgd dbsp</td>
<td></td>
</tr>
<tr>
<td>24466</td>
<td>0.8 Co</td>
<td>0.20</td>
<td>bgd dbsp</td>
<td>big reactor filamentous; easy to mount</td>
</tr>
<tr>
<td>24467</td>
<td>2.64 Co</td>
<td>1.00</td>
<td>bgd dbsp</td>
<td>pmC 0.58±0.02</td>
</tr>
<tr>
<td>24468</td>
<td>1.43 Co</td>
<td>1.00</td>
<td>bgd dbsp</td>
<td>pmC 0.54±0.02</td>
</tr>
<tr>
<td>24469</td>
<td>0.66 Co +0.90 Cr</td>
<td>1.00</td>
<td>bgd dbsp</td>
<td>Cu cut, but could be removed from the cathode pmC 0.55±0.02</td>
</tr>
<tr>
<td>24470</td>
<td>0.39 Co</td>
<td>0.20</td>
<td>bgd dbsp</td>
<td>fine powder; easy to mount</td>
</tr>
<tr>
<td>24471</td>
<td>1.38 Co</td>
<td>0.20</td>
<td>bgd dbsp</td>
<td>one compact piece, some powder easy to crush and to mount</td>
</tr>
<tr>
<td>24472</td>
<td>2.53 Fe</td>
<td>0.97</td>
<td>bgd wood</td>
<td>easy to crush and to mount</td>
</tr>
<tr>
<td>24473</td>
<td>0.55 Fe</td>
<td>1.01</td>
<td>bgd wood</td>
<td>mounted again with more silver half of it fell out (stuck to Cu)</td>
</tr>
<tr>
<td>24474</td>
<td>0.67 Fe +1.58 Cr</td>
<td>0.97</td>
<td>bgd wood</td>
<td>powder with some chunks easy to crush some fell out light spots visible on surface</td>
</tr>
<tr>
<td>24475</td>
<td>0.84 Fe</td>
<td>1.06</td>
<td>bgd wood</td>
<td>graphite like 24474 some fell out, some stuck to Cu</td>
</tr>
<tr>
<td>24476</td>
<td>0.83 Fe</td>
<td>0.95</td>
<td>Gel A</td>
<td>graphite like 24474 fell out (stuck to Cu) mounted again with more silver most of the graphite fell out mounted again without more silver</td>
</tr>
<tr>
<td>24477 and 24478</td>
<td>2.0 Fe</td>
<td>0.93</td>
<td>Gel A</td>
<td>fell out (stuck to Cu) mounted again without more silver and with lower pressure</td>
</tr>
<tr>
<td>24479</td>
<td>0.19 Fe</td>
<td>0.99</td>
<td>Gel A</td>
<td>powder with some chunks some fell out, some stuck to Cu</td>
</tr>
<tr>
<td>24480</td>
<td>&lt;2 Fe</td>
<td>0.19</td>
<td>bgd wood</td>
<td>some iron couldn’t be taken out one compact piece, hard to crush hard to mount, but finally ok</td>
</tr>
<tr>
<td>24481</td>
<td>0.34 Fe</td>
<td>0.19</td>
<td>bgd wood</td>
<td>not all could be taken out half of the graphite fell out mounted again; silver visible</td>
</tr>
</tbody>
</table>

Table 4.10: Mounting of graphite-catalyst mixture in cathodes
4.3.2 Stable isotope measurements

To quantify the fractionation resulting from graphitisation, samples for $\delta^{13}\text{C}$ measurements were taken from different steps in the combustion-graphitisation procedure (cf. Figure 2.4). Stable carbon isotope ratios, $\delta^{13}\text{C}$, can be measured either on solids (EA-CN) or on $\text{CO}_2$ (DI). It is thus possible to measure the fractionation during graphitisation with first measuring $\delta^{13}\text{C}$ (DI) on the $\text{CO}_2$ and then $\delta^{13}\text{C}$ (EA-CN) on the graphite (figure 4.18). For this purpose, the graphite-catalyst mixture was homogenized and weighed out into tin capsules.

To measure the effect of graphitisation only, with excluding effects from combustion, a large amount (20.52 mg) of the standard material Ox-I was combusted in an evacuated quartz tube with 200 mg CuO, and yielded $\text{CO}_2$ corresponding to 4.06 mgC (19.8%). This $\text{CO}_2$ was divided into 9 subsamples for graphitisation and one for DI-$\delta^{13}\text{C}$ measurement. All subsamples were graphitised in big reactors, two in small reactors (one of these two was lost when the graphitisation tube broke). The $\delta^{13}\text{C}$ value of the gas, measured with the DI method (cf. chapter 3), was -19.18‰, very close to the standard value of -19‰ (Table 4.5). The $\delta^{13}\text{C}$ values of the graphite, measured with the EA method, are given in table 4.11. Four of the $\delta^{13}\text{C}$ values were extremely low, and these were those with the lowest carbon fractions and the lowest peak heights in the mass spectrometer. They are therefore excluded from further analysis.

In figure 4.19, the $\delta^{13}\text{C}$ value measured on $\text{CO}_2$ is indicated by a red line. It is close to the standard value of -19‰. Blue diamonds denote $\delta^{13}\text{C}$ measurements on graphite plotted against the amount of $\text{CO}_2$ graphitised. This figure shows that the fractionation is larger for smaller graphitised amounts. The exception is the smallest sample, with 0.15 mgC, which lies closest to the $\text{CO}_2$ $\delta^{13}\text{C}$-value. This was in fact the only sample that had been graphitised in a small reactor; all the other samples were graphitised in normal-sized reactors. The smaller reactor volume thus prevents the increase of fractionation for small samples.

Figure 4.20 displays the fractionation (i.e. the deviation of the $\delta^{13}\text{C}$ of the graphite from the standard values) for different graphitisations in big and small reactors with cobalt and iron catalysts and emphasizes the importance of small reactors to minimize fractionation in small samples. From this figure, it is difficult to tell whether iron or cobalt is the best catalyst, as both can introduce large fractionation for small samples.

4.3.3 Radiocarbon dating

$^{14}\text{C}$ dating was performed to assess the amount of contamination. Modern contamination can be detected by dating background ($^{14}\text{C}$-free) samples, old contamination by dating modern samples, e.g. Oxalic acid. Unfortunately, some samples could not be measured. Cathodes had been prepared, so the graphite could not be sent to another laboratory for radiocarbon dating. Table 4.12 gives an overview of these samples.

Radiocarbon datings of samples graphitised with the different settings are shown in figure 4.21. The data are given in percent modern carbon, pmC. The background values (figure 4.21a) for small samples in small reactors are slightly better (i.e., lower) than those for a normal-sized sample in a big reactor. Usually, background values are expected to be worse for smaller samples, assuming a constant amount of modern contamination that is added to the sample during preparation. It can also be seen that iron gives better background levels than cobalt.

Figure 4.21b shows pmC determinations of oxalic acid (both Ox-1 and Ox-2), given as deviation from the respective standard values. From the few measurements displayed here, I cannot decide whether iron or cobalt gives the better oxalic acid values: six of the samples graphitised on cobalt have better, two of them inferior values to the samples graphitised on iron.

4.4 Conclusions

Although many measurements could not be finished, some recommendations can nevertheless be made.

The $\text{CO}_2$ collected with an additional step of trapping and pressure measurement is a good representation of the sample’s carbon, both regarding $\delta^{13}\text{C}$ measurement and $^{14}\text{C}$ dating. However, possible memory effects have to be examined further, and the yield is too low and variable.

For $\text{CO}_2$ trapping, tube diameters should be kept as small as possible when constructing a cryogenic trap. If a zeolite trap is used, a pre-cleaning procedure immediately prior to trapping should be performed. Furthermore, opening and closing of the trap valves should be controlled electronically and take place after a fixed period past sample combustion, as the trapping time seems to be vital for the zeolite trap.

The fractionation during quartz tube combustion could not be quantified, and it is not clear whether the fractionation is larger for smaller samples, as the results from different tests are ambiguous. The CuO used in quartz tube combustion is a signifi-
4.4. CONCLUSIONS

Figure 4.18: Assessment of fractionation during graphitisation: sampling for $\delta^{13}$C measurements.

<p>| graphitisation | transferred to | tin cup | sample | $\delta^{13}$C |</p>
<table>
<thead>
<tr>
<th>SSID</th>
<th>reactor (mgC)</th>
<th>SSID</th>
<th>weight (mg)</th>
<th>(%) VPDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>48674</td>
<td>0.99</td>
<td>48736</td>
<td>0.196</td>
<td>-21.16±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48737</td>
<td>0.229</td>
<td>-20.37±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48738</td>
<td>0.201</td>
<td>-20.26±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48739</td>
<td>0.179</td>
<td>-20.31±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48740</td>
<td>0.195</td>
<td>-20.89±0.17</td>
</tr>
<tr>
<td>48675</td>
<td>0.79</td>
<td>48741</td>
<td>0.346</td>
<td>-17.32±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48742</td>
<td>0.112</td>
<td>-20.17±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48743</td>
<td>0.227</td>
<td>-20.38±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48744</td>
<td>0.267</td>
<td>-21.28±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48745</td>
<td>0.174</td>
<td>-21.65±0.17</td>
</tr>
<tr>
<td>48676</td>
<td>0.59</td>
<td>49066</td>
<td>0.497</td>
<td>-40.26±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49067</td>
<td>0.248</td>
<td>-39.89±0.1</td>
</tr>
<tr>
<td>48677</td>
<td>0.4</td>
<td>48748</td>
<td>0.247</td>
<td>-21.15±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48749</td>
<td>0.326</td>
<td>-21.3±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48750</td>
<td>0.365</td>
<td>-21.5±0.1</td>
</tr>
<tr>
<td>48678</td>
<td>0.35</td>
<td>48751</td>
<td>0.537</td>
<td>-23.03±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48752</td>
<td>0.436</td>
<td>-23.87±0.1</td>
</tr>
<tr>
<td>48679</td>
<td>0.2</td>
<td>48753</td>
<td>0.48</td>
<td>-25.44±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48754</td>
<td>0.211</td>
<td>-25.81±0.1</td>
</tr>
<tr>
<td>48680</td>
<td>0.15</td>
<td>48755</td>
<td>0.576</td>
<td>-36.53±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>48733</td>
<td>0.78</td>
<td>-18.67±0.1</td>
</tr>
<tr>
<td>48682</td>
<td>0.15</td>
<td>48733</td>
<td>0.78</td>
<td>-18.67±0.1</td>
</tr>
</tbody>
</table>

Table 4.11: Combustion of a large Ox-I sample and graphitisation of different amounts of the resulting CO$_2$.

A significant potential source of contamination because large amounts (200 mg) are used (Alderliesten et al., 1998). However, a reduction of the CuO amount to adapt the combustion for small samples is problematic and leads to large deviations from the standard values. A possible solution is combustion at the EA with CO$_2$ collection as presented in section 4.1.

For the graphitisation of samples below 0.25 mgC, small reaction volumes should be used. This enhances graphitisation characteristics and reduces fractionation. However, radiocarbon dating of graphite from small reactors must still be tested, and e.g. background levels must be determined, before the small reactors are recommended for routine sample preparation (cf. table 4.12). The few background samples from small reaction volumes have unsatisfactory background levels (see figure 4.21 and chapter A in the appendix).
CHAPTER 4. IMPROVEMENTS OF SAMPLE PREPARATION TECHNIQUES

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSID</th>
<th>C-nr.</th>
<th>sample size, graphitisation parametres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-I</td>
<td>22075</td>
<td>19792</td>
<td>550°C, Fe</td>
</tr>
<tr>
<td>bgd bone</td>
<td>23079</td>
<td>19924</td>
<td>should have been measured together with C-20496, C-20497, C-19754</td>
</tr>
<tr>
<td>bgd bone</td>
<td>23082</td>
<td>19931</td>
<td>little reactor, 0.087mgC</td>
</tr>
<tr>
<td>std humic acid</td>
<td>23157</td>
<td>19963</td>
<td>1.13mgC</td>
</tr>
<tr>
<td>Gel A</td>
<td>23189</td>
<td>19970</td>
<td>1.05 mgC</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>23251</td>
<td>19987</td>
<td>small reactor, small cathode, 0.202mgC</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>23252</td>
<td>19988</td>
<td>small reactor, small cathode, 0.087mgC</td>
</tr>
<tr>
<td>bgd wood</td>
<td>23072</td>
<td>20079</td>
<td>small reactor, 0.120mgC</td>
</tr>
<tr>
<td>Gel A</td>
<td>24087</td>
<td>20096</td>
<td>1.17 mgC, combusted with silver, Fe 550°C</td>
</tr>
<tr>
<td>bgd gw</td>
<td>24126</td>
<td>20048</td>
<td>0.042 mgC, small reactor, small cathode</td>
</tr>
<tr>
<td>bgd gw</td>
<td>24127</td>
<td>20049</td>
<td>0.042 mgC, small reactor, small cathode, Fe 530°C</td>
</tr>
<tr>
<td>Gel A</td>
<td>24588</td>
<td>20129</td>
<td>0.11 mgC</td>
</tr>
<tr>
<td>Gel A</td>
<td>24589</td>
<td>20130</td>
<td>0.2024 mgC</td>
</tr>
<tr>
<td>Gel A</td>
<td>24590</td>
<td>20133</td>
<td>0.64005 mgC</td>
</tr>
<tr>
<td>Gel A</td>
<td>24591</td>
<td>20134</td>
<td>0.12684 mgC</td>
</tr>
<tr>
<td>bgd bone</td>
<td>24800</td>
<td>20168</td>
<td>0.04032 mgC BP; Small cathode, hammered; not much graphite visible (P_end very high, although reaction was finished).</td>
</tr>
<tr>
<td>bgd bone</td>
<td>24801</td>
<td>20169</td>
<td>0.05628 mgC BP; Small cathode, hammered.</td>
</tr>
<tr>
<td>Gel A</td>
<td>50136</td>
<td></td>
<td>0.85 mg Fe</td>
</tr>
<tr>
<td>Gel A</td>
<td>50137</td>
<td></td>
<td>2.0 mg Fe</td>
</tr>
<tr>
<td>Gel A</td>
<td>50139</td>
<td></td>
<td>0.52 mg Fe</td>
</tr>
<tr>
<td>Gel A</td>
<td>50140</td>
<td></td>
<td>0.19 mg Fe</td>
</tr>
</tbody>
</table>

Table 4.12: Cathodes that could not be measured because they had waited too long for the accelerator to work again.

Figure 4.19: Combustion of a large Ox-I sample and graphitisation of different amounts of the resulting CO₂.
Figure 4.20: Graphitisation in big and small reactors, with cobalt and iron as catalysts.

Figure 4.21: pmC and pmC deviations for background samples and the oxalic acid standards Ox-1 and Ox-2. Black symbols indicate graphitisation on cobalt, red symbols graphitisation on iron. 1: big reactor, 2: small reactor. Note that the background level of the large sample, graphitised with cobalt, is unusually high. Normally, the same levels as for iron are achieved.
Figure 4.22: pmC deviations for background samples (bgd gw, bgd db sp, bgd anthracite) and standards (Ox-I and Gel A).
Chapter 5

Nature and Culture in Eurasia during the Holocene

The aim of this chapter is to create a framework for the studies presented in chapter 6 and 7, which are about radiocarbon dating of the earliest pottery in Northern Germany, the development of the Limfjord in Northern Denmark and about variability of reservoir effects in freshwater and estuarine systems.

The information about palaeoclimate, the development of environment and human cultures since the end of the last glacial period fills libraries and an all-embracing presentation would go beyond the scope of this chapter – even when concentrating only on Eurasia. I will thus only follow two space-time trajectories when describing the mutual interaction between people and their environment, between nature and culture. The first trajectory proceeds in time, at constant space co-ordinate, and follows the development of climate and environment in Northern Europe, concentrating on Denmark and Northern Germany with the surrounding seas (North Sea, Skagerrak, Kattegat, Baltic) from the end of the last glacial period until today. The second trajectory advances both in time and space and follows the oldest pottery among hunter-gatherer groups from the Eastern fringe of Eurasia (Japan, China and Russia’s far east), where it originated after 20,000 cal BP (18,000 BC), until it encounters the first trajectory with the introduction of pottery in Schleswig-Holstein in the Ertebølle culture, 5400-4000 BC (7400-6000 cal BP). The pottery trajectory begins thus in time before the start of the Holocene, i.e. around the last glacial maximum.

Although the first trajectory focuses on the natural environment and the second on a cultural phenomenon, both aspects are intrinsically tied to each other, as humans adapt to their natural environment, while all human activities also influence the environment.

5.1 Terms, concepts and chronologies

If not noted otherwise, the definitions presented here are based on Roberts (1998). I will describe phases and nomenclature as they are common in Northern Europe. Ages will mainly be given as calibrated ages BP, cal BP, according to the tradition in climate research, for climatological and environmental developments as well as for the oldest pottery. BP denotes here “before present” and means “before AD 1950”. Cultural developments will mostly be dated as calibrated ages BC/AD. However, in most cases I try to give the alternative format as well. For better readability, numbers equal to and higher than 10,000 will be given with a comma separator, numbers equal to and below 9999 without.

The most recent geological period, from about 2.6 million years BP until today, is called the Quaternary. It spans the era of anatomically modern humans and is divided into the Pleistocene and Holocene. The Pleistocene is characterized by repeated glaciations. The Saalian stage, 300,000-130,000 BP, included 2-3 glaciations. Denmark and the entire North German Plain were covered by glaciers (Henningsen and Katzung, 1992). After the Eemian warm period, the Weichselian glaciation began in ca. 115,000 BP. During this glaciation, western Jutland and western Schleswig-Holstein were ice-free. The Last Glacial Maximum with minimum sea levels was in ca. 25,000-13,000 cal BP.

The end of the Weichselian glaciation was characterized by some temperature fluctuations between relatively warm periods (interstadials) and cold periods (stadials). Each of these stages only lasted between several hundred and up to thousand years. Beginning with the oldest, these are the Belling interstadial, the Older Dryas stadial, the Allerød interstadial and, fi-
nally, the Younger Dryas stadial which marks the end of the Weichselian period and thus the end of the Pleistocene.

The Holocene begins after the end of the last glaciation, ca. 12,000 - 10,000 cal BP, and lasts until today. The dating of the onset of the Holocene depends on which region is examined and what climatic proxy is used for finding the timing of the end of the glacial period. It has also been suggested to define the beginning of the Holocene as 10,000 \(^{14}\)C years BP. However, as the calibration curve has a plateau at 10,000 \(^{14}\)C years BP, this \(^{14}\)C level does not define a moment in time, but a period of about 400 years (Figure 2.2). A consensus value is the dating found in ice core records of \(\delta^{18}\)O values, 11,703±99 b2k (“before AD 2000”, Rasmussen et al., 2006, see figure 5.6). The Holocene is a period of relatively stable climate in Europe, compared to the glacial and interglacials of the preceding Pleistocene. The Holocene is divided into climatic stages, the so-called Blytt-Sernander stages, and pollen zones (see table 5.1). As deficiencies were found in the original scheme, and vegetational changes can be time-transgressive, the Blytt-Sernander stages are falling into disuse, although they still are used colloquially.

The oldest form of human economy is hunting, fishing, and gathering (hfg). In many regions of the world, it was practiced throughout the major part of the Holocene. However, the Holocene also witnessed one of the most important changes in human subsistence, the introduction of agriculture and domestication. In some regions, it was followed by the first cities and civilizations.

Human cultural development has been divided into three big phases, according to the primary raw material for the production of tools. These are the Stone Age, Bronze Age, and Iron Age. When these transitions occurred varies by locality, and also the subdivision between the phases differs in different regions of the world.

Worsaae (1859) analysed Danish finds and discovered that the Stone Age can be divided into two parts. The older Stone Age, with coarsely knapped flint tools and kitchen middens, could also be found in caves in England and France associated with remains of extinct animal species. The younger Stone Age was characterised by polished axes and megalithic graves. In the beginning, this idea was criticised, as the tools could have been manufactured contemporaneously, but for different purposes Steenstrup (1859). However, today there is general agreement that the Stone Age can be divided into an older and younger part. They are termed Palaeolithic and Neolithic after the Greek παλαιός, “old”, νέος, “new”; and λίθος, “stone”. In many regions, a transition phase between the Palaeolithic to the Neolithic is recognized and termed, depending on local tradition, Epipalaeolithic or Mesolithic. Although “Epipalaeolithic” and “Mesolithic” can be used synonymously, the first term usually describes cultures in regions unaffected by glaciation. The latter is used extensively in Northern Europe to describe post-Glacial hunter-fisher-gatherer (hfg) groups after the European megafauna extinction who utilise tools made of small flint flakes, the so-called microliths.

The beginning of the Neolithic is the incorporation of one or more elements of the “Neolithic package” into the region, e.g. agriculture, animal husbandry, pottery, polished (in contrast to chipped) stone tools, sedentariness and/or urbanization. In Eastern Europe, for example, the onset of the Neolithic is defined as the first occurrence of pottery, while in Northwestern Europe, the focus is on subsistence strategy (Jordan and Zvelebil, 2009). Taken to extremes, a hfg group producing pottery would thus belong to the Mesolithic if it was found west of the modern German-Polish border, but Neolithic, if it was found east of that border. As the above-mentioned cultural phenomena can occur in different combinations, phases like a pre-pottery Neolithic, pre-agricultural Neolithic or a ceramic Mesolithic can be defined.

The cultural phases which are distinguished in the study area, Denmark and northernmost Germany, are presented in table 5.2. Due to the global eustatic sea level rise after the end of the last glacial period (see section 5.2), many Mesolithic sites are now submerged. As the oldest coastal sites lie deepest under the sea, they are hardest to find. Large coastal settlements from the beginning of the Kongemose culture have been found, e.g. on the bottom of the Storebælt (Fischer, 1997b), and coastal sites from the Maglemose culture may have existed, but lie now several meters below present sea level. Earlier cultures include the Hamburg culture at the end of the Weichselian glaciation, the subsequent Bromme culture during the Allerød interstadial and the Ahrensburg culture, during the Younger Dryas. These were specialized reindeer or elk hunters and are mainly known from stray finds and occasional small settlement sites in Denmark and Northern Germany.
5.2. THE NORTHERN EUROPEAN CLIMATE TRAJECTORY

The information in this section, if not indicated otherwise, is from (Roberts, 1998) and Lowe and Walker (1997). After the end of the glaciation, Eurasia witnessed a series of environmental changes that directly affected human populations. These include megafauna (e.g. mammoth) extinction, global eustatic sea-level rise, reforestation, and soil formation.

Lateglacial climatic oscillations include the end of the Glacial about 15,000 cal BP, the warm Bølling / Allerød Interstadial until 13,000 cal BP, the cold Younger Dryas Stadial after that, and finally, from about 11,500 cal BP, the early Holocene. Although the Holocene is a period of relatively stable climate, some minor changes have been identified. The Holocene thermal optimum, ca. 9000-5500 cal BP, was followed by a stepwise cooling. One step of climate deterioration was the transition from the Sub-Boreal to the Sub-Atlantic (table 5.1) which happened in Europe in about 2600 cal BP. The Roman Warm Period from ca. 250 BC to AD 400 facilitated the Roman expansion, as it became easier to cross the Alps, or to grow wine in England. The warm period was followed by a minor cooling until ca. AD 750 where the climate in Europe was wetter and the winters cooler. During the Medieval Warm Period, AD 950-1250, Iceland and Greenland were settled. The Little Ice Age is known for e.g. ice fairs on the river

### Table 5.1: The Blytt-Sernander stages and pollen zones for the European Holocene

<table>
<thead>
<tr>
<th>Period</th>
<th>Pollen zone</th>
<th>Inferred climate</th>
<th>Approx. age cal. BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Boreal</td>
<td>IV</td>
<td>cool/dry</td>
<td>11,500-10,500</td>
</tr>
<tr>
<td>Boreal</td>
<td>V/VI</td>
<td>warm/dry</td>
<td>10,500-7800</td>
</tr>
<tr>
<td>Atlantic</td>
<td>VIIa</td>
<td>warm/wet</td>
<td>7800-5700</td>
</tr>
<tr>
<td>Sub-Boreal</td>
<td>VIIb</td>
<td>warm/dry</td>
<td>5700-2600</td>
</tr>
<tr>
<td>Sub-Atlantic</td>
<td>VIII</td>
<td>cool/wet</td>
<td>2600-present</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Age cal. BP</th>
<th>Age BC/AD</th>
<th>Culture</th>
</tr>
</thead>
<tbody>
<tr>
<td>10950/10550-8450/8350</td>
<td>9000/8600-6500/6400</td>
<td>Maglemose culture; settlements mainly at rivers and lakes</td>
</tr>
<tr>
<td>8450/8350-7350/7150</td>
<td>6500/6400-5400/5200</td>
<td>Kongemose culture; the earliest coastal sites</td>
</tr>
<tr>
<td>7350/7150-5950/5900</td>
<td>5400/5200-4000/3950</td>
<td>Ertebølle culture (EBK)</td>
</tr>
<tr>
<td>5950/5900-3750/3650</td>
<td>4000/3950-1800/1700</td>
<td>Neolithic; introduction of agriculture; same settlement sites as in the Ertebølle culture, hunting and fishing stations still in use, but also new sites on light soils where cereals were grown</td>
</tr>
<tr>
<td>5950/5900-4750</td>
<td>4000/3950-2800</td>
<td>Funnel Beaker culture (TRB)</td>
</tr>
<tr>
<td>5150-4250</td>
<td>3200-2300</td>
<td>Pitted Ware culture (PWC), a hunter-fisher-gatherer culture in southern Scandinavia</td>
</tr>
<tr>
<td>4750-4350</td>
<td>2800-2400</td>
<td>Single Grave culture (EGK)</td>
</tr>
<tr>
<td>4350-3750/3650</td>
<td>2400-1800/1700</td>
<td>Late Neolithic Dagger Culture; trade connections with the rest of Europe are intensified and metal objects are imported</td>
</tr>
<tr>
<td>3750/3650-2450</td>
<td>1800/1700-500</td>
<td>Bronze Age; animal husbandry and agriculture are the main subsistence strategies</td>
</tr>
<tr>
<td>3750-2950</td>
<td>1800-1000</td>
<td>Older Bronze Age</td>
</tr>
<tr>
<td>2950-2450</td>
<td>1000-500</td>
<td>Younger Bronze Age</td>
</tr>
<tr>
<td>2450-1200</td>
<td>500 BC - AD 750</td>
<td>Iron Age</td>
</tr>
<tr>
<td>2450-1950</td>
<td>500-0</td>
<td>Plerom Roman Iron Age</td>
</tr>
<tr>
<td>1950-1550</td>
<td>AD 0-400</td>
<td>Roman Iron Age</td>
</tr>
<tr>
<td>1550-1200</td>
<td>AD 400-750</td>
<td>Germanic Iron Age</td>
</tr>
</tbody>
</table>

Table 5.2: Cultural phases in Denmark. This division also applies to Northern Germany, though partly with slightly different dates. After Andersen (1986, 1990); Fischer (2002a).
Thames in London. It lasted from AD 1590-1850 and brought a drop in temperature of ca. 1°C – not very much, compared to the 10°C drop of the Pleistocene.

### 5.2.1 Sea level

During the Last Glacial Maximum, the global sea level was up to 120 m lower than at present (Fairbanks, 1989). During the first ca. 1000 years of the Holocene, temperatures rose to approximately modern values. Glaciers and ice-sheets melted correspondingly. The smallest ice-masses disappeared first, while the Laurentide ice sheet in northern America remained extensive until ca. 9000 cal BP. The period from the end of the last glacial period until ca. 9000 cal BP/7000 BC is also called the “Continental Period”, fastlandstiden, in Denmark, as the western Baltic Sea and much of the Kattegat and North Sea formed a continuous forest-covered land mass (Christensen et al., 1997; Noe-Nygård et al., 2006).

With the end of the glaciation, meltwater caused the global sea level to rise (“eustatic sea-level rise”), until modern levels were reached ca. 7000–6000 years ago. A lot of forest was covered by the sea, often after the trees had died because of rising groundwater levels. Trunks that soon after were covered by oxygen-depleted sea water or mud are preserved until today. In the Storebelt, for example, a pine forest from around 10,000 cal BP was found at a water depth of 30 m, while a submerged forest at 8 m depth contained lime tree and alder, which had died in the centuries around 8300 cal BP (Fischer, 1997a). The North Sea developed in 10,000 to 8000 cal BP, and the coast line moved on average 100 m per year, so that settlements had to be relocated frequently (Lüth et al., 2004). The sea level rise resulted since 9000 cal BP in the transition of the freshwater-filled Ancylus Lake to a marine environment on the location of the Baltic Sea (Björck, 1995, 2008). The new sea is also termed the Littorina Sea after the salt water snail称呼为“Littorina Sea”.

Several “Littorina transgressions” can be identified (Christensen, 1995; Noe-Nygård et al., 2006). At Vælby, for example, four Littorina transgressions were dated to 7200, 6700, 6200 and 5700 cal BP (Blankholm, 2008). They are termed the Early Atlantic, High Atlantic, Late Atlantic and Subboreal Transgressions (Noe-Nygård et al., 2006).

Figure 5.1 shows an early account of the maximum expansion of the sea in Northern Jutland in the Stone Age.

The maximum sea level in the Littorina Sea occurred around 7500 cal BP when salinity was 6–8% higher, and the water volume in the Baltic proper almost 50% larger than today (Lougheed et al., 2012, and references therein). The Danish fjords of the Littorina Sea were more saline and nutrient-rich than today, possibly a consequence of a higher tidal amplitude (Noe-Nygård et al., 2006; Iverson, 1967a).

Details about the development of the Baltic Sea can be found in Björck (1995, 2008). The formation of the Baltic Sea resulted in a wide variety of habitats, with estuarine systems being the most stable and diversified ones (Mahler, 1981). Around 9000-8000 cal BP, the Danish sounds like the Storebelt were formed (Christensen et al., 1997). From then on, the sea level was relatively stable on large parts of the Earth and coastlines took on their modern form (Roberts, 1998). Today’s marshlands on the western coast of northern Germany and south-western Denmark were part of the North Sea in 5000 BC (7000 cal BP). A spit coast developed, and some of the spits were used as settlement sites by e.g. the Ertebølle culture (see below Arnold, 1991). Large shell middens are basically unknown before ca. 7000-6000 cal BP as a stable coast line is a precondition for the anthropogenic accumulation of shells over centuries (Bailey, 2007).

At the same time, land masses that had been weighed down by ice sheets began to rise, a process that is called “isostatic rebound”. In areas like northern Scandinavia, the isostatic land rise could be much larger than the eustatic sea level rise. The resulting modern sea levels are thus actually lower than at the beginning of the Holocene. ΔR in the Littorina Sea decreased accordingly from about 400 years in 7000 cal BP to -200 years in 1000 cal BP, as freshwater with low reservoir ages dominated increasingly (Lougheed et al., 2012). Around the areas that had been pushed down by the weight of the ice, in contrast, there were zones that had been pushed up during the Glacial. These zones now started to “rebound downwards”, as the isostatic uplift took place in areas freed from their ice cover (Roberts, 1998). After the end of global eustatic sea level rise around 6000 cal BP, isostatic adjustments became dominant in governing local sea levels. In the north of Denmark, isostatic rebound finally dominated, while the south of Denmark and Northern Germany have experienced rising sea levels until today. The border between these two phenomena is called the “vippelinie”, the tilt line, in Danish, and is indicated by the zero-isobase on the map by Mertz (1924), figure 5.2. On this line, there had been no land rise or sea level rise since the last glacial period, only small changes in sea level due to fluctuations in world climate (Christensen et al., 1997). Figure 5.3 summarizes the information about the Littorina Sea.

North of the tilt line, sea level has thus decreased since the Stone Age, as the land rose. The Limfjord,
5.2. THE NORTHERN EUROPEAN CLIMATE TRAJECTORY

a sound through Northern Jutland, illustrates this development: What today is a continuous land mass north of the Limfjord had been an archipelago 6000 years ago. Stone Age settlements north of the tilt line are today accessible on land and can lie several metres above present sea-level. Stone Age settlements in southern Denmark and Northern Germany, however, south of the tilt line, are today submerged and can be several metres under water. This makes the sites more difficult to find and excavate, but results in excellent preservation of organic materials. One example of such a submerged settlement is the site Neustadt in Northern Germany (see chapter 6).

As an example north of the vippelinie, the effect of the isostatic rebound on the Limfjord region is illustrated in figure 5.4. In these figures, a uniform sea level development was assumed for the whole Limfjord region. The actual sea level had been even higher in the Northern Limfjord region, than in the south.

Some other effects are not represented in figure 5.4. The Western part of the Limfjord, for example, had been closed off from the North Sea by the “Jutland Bank”. The region north of the Limfjord, in contrast, had been even more open before aeolian and fluvial transport deposited substantial amounts of sand.
Figure 5.1: The maximum expansion of the Stone Age sea. From Jessen (1920).
Figure 5.2: Map of late- and postglacial sea level changes in Denmark. Mertz (1924). For a drawing of the maximum sea levels of the Littorina Sea only, see figure 5.3.
Figure 5.3: Isobases for the maximum levels of the Littorina Sea, redrawn by Krog (1979) after Mertz (1924).
5.2. THE NORTHERN EUROPEAN CLIMATE TRAJECTORY

Figure 5.4: Relative sea-level changes in the Limfjord region. By Jesper Olsen.
5.2.2 Flora and Fauna

During the glacial, the ice-free regions of Europe were covered by tundra-steppe and boreal forest. Around 15,000 cal BP, Northern Jutland, for example, was a tundra landscape characterised by dwarf birch, polar willow, juniper, dryas, crowberry, sea-buckthorn, herbs and grasses. It supported reindeer, horse, bison, elk, bear, wolverine, beaver, snow hare and polar bear (Andersen, 1986; Noe-Nygård et al., 2006).

This changed after 11,500 cal BP when deciduous trees returned to Europe. From ca. 10,500 cal BP, trees also returned to Northern Jutland, first pioneer species like birch and pine, later hazel, elm, fraxinus, oak and lime (Andersen, 1986). By 9000 cal BP, the dominant vegetation type in Europe had become deciduous forest, but also wetlands had increased. The species composition of these forests, however, was still subject to changes. Many plant species had survived the glaciation in refugia south of the Alps. Therefore, some plants returned to Denmark a long time after the climatic conditions had become suitable for them (Noe-Nygård et al., 2006). During the first 5000 years after the last glaciation, the soil, the climate and the competition and spread of trees governed the composition of the forest (Aaby, 1993a). Together with the megafauna extinction during the late Glacial, this change in vegetation required a change in subsistence strategy from the prehistoric Europeans. Instead of following large herds of horse or reindeer on the open steppe plains, people hunted for example red deer with bow and arrow in the deciduous woodland. The woodland animals were more dispersed and less visible. Edible plant species, however, became much more numerous and could be collected with less effort than their hunted meat equivalent (Roberts, 1998). Sites were often located close to fresh-water environments where edible plant species such as cress and water lily (Clarke, 1978) could be exploited alongside fish and shellfish.

In 9500-7000 BP, δ13C values of human bones from southern Scandinavia indicate that human diet had been mainly terrestrial. However, at this time, the Baltic basin transformed from the Ancylus lake to the Littorina sea, and a marine signature cannot be expected for people who lived on resources from the Baltic during the Ancylus stage (Ahlström, 2003). After 7000 BP, however, all human bone δ13C values can be considered marine (Ahlström, 2003).

The first indicators of deliberate anthropogenic vegetation transformations are from the late Mesolithic. They include forest clearances, probably by fire (Roberts, 1998) or ringing, where the bark and phloem are cut, resulting in the death of the tree (Iversen, 1967b). Also the management of hazel coppicewood could be reconstructed (Christensen, 1997). Forest regrowth after clearances enhances browsing and grazing potential and attracts animals like deer. Hazel provides hazelnuts and straight branches for the construction of e.g., permanent fishing constructions. Coppiced lime-tree was used as well for stakes and withes for fish weirs (Christensen, 1997). Forest clearance had thus multiple benefit for the Mesolithic population, and the primary reason for clearances is difficult to identify. The felling of large trees for firewood, however, can be excluded. Analysis of Stone Age fireplaces showed that mainly small branches were used (Malmros, 1997).

At the transition between Atlantic and Subboreal, pollen diagrams all over Northern Europe show a distinct decline in elm pollen. This has been explained as a result of decreasing temperature, elm disease, anthropogenic forest clearances or the use of elm as leaf fodder (Noe-Nygård et al., 2006; Odgaard, 2006; Iversen, 1949, 1967a). The uniformity of the elm decline all over Northern Europe is an argument against anthropogenic causes. However, climatic reasons seem unlikely as the elm decline also occurred in regions that still were warm enough to support elm (Iversen, 1967a). The most likely explanation is a combination of the above-mentioned factors that all interacted to weaken the elm.

The introduction of agriculture around 6000 cal BP (4000 BC) is recorded in pollen diagrams as the decline of trees and increasing amounts of pollen from herbs and grasses, especially sorrel and plantain. Early cereals were self-pollinators and are therefore difficult to observe in pollen diagrams (Iversen, 1949).

Middle and Late Holocene vegetation changes are to a larger extent anthropogenic and can mask e.g., the climate cooling around 2600 cal BP; anthropogenic and climate causes are difficult to discern. Agriculture can lead to vegetation degradation, as a result of soil erosion and deforestation. However, early agriculture also created new habitats and a more varied landscape, providing ecological niches for new plant species.

In the Bronze Age (see table 5.2), Denmark was still covered with primeval forest, although clearances and pasture for cattle had become more common (Andersen, 1986). With the beginning of the Iron Age in about 500 BC, 2450 cal BP, the climate in Denmark became cooler and more humid. Together with anthropogenic deforestation, this facilitated the invasion of a new tree species, the beech (Andersen, 1986).

Since the Iron Age, or perhaps already since the
5.3. THE HUNTER-GATHERER POTTERY TRAJECTORY

Late Bronze Age, permanent field systems were used in Denmark. The square Early Iron Age fields disappear in AD 100-200. In AD 1200, the so-called ridge-and-furrow fields appear (Aaby, 1993b). This system, before the introduction of artificial fertiliser, could support 50-300 people per km² (Aaby, 1993b).

During the last 500 years, anthropogenic environmental change has accelerated because of mechanization in agriculture, accelerated urbanisation and increasingly exploitative economies. European colonialism had not only a substantial impact on the lives of people throughout the world, but also on vegetation on numerous continents, mainly by spread of species, but also by the introduction of new modes of production, forest clearances and extinction of species. Two of the present-day main crops in Denmark and Northern Germany, maize and potatoes, were introduced after their “discovery” in the New World.

5.3 The Hunter-Gatherer pottery trajectory

First, I will give a review of theories that try to explain how and why pottery was invented, and consider its possible benefits for nutrition. I will focus on pottery in the sense of ceramic containers for food preparation or storage, as other ceramic artefacts, e.g. baked clay figurines, seem to be an unrelated phenomenon. I will then follow the spread of pottery from the presumed origins in East Asia to central Europe, where it accompanied hunter-fisher-gatherer groups. I will also mention pottery in early farming cultures, as it is speculated that Ertebølle pottery was influenced by these as well (e.g. Andersen, 1973).

5.3.1 The origins of pottery

The phenomenon of baked clay must have been well-known for humankind since the first fireplaces were built and clay-rich soils next to them were unintentionally fired (Hoopes and Barnett, 1995). The control of fire might already be 1.8 million years old (Wrangham, 2009), so in theory, already *Homo erectus* might have observed the accidental formation of “ceramics”.

In central Europe, the first clay figurines were made in 28,000-22,000 cal BP (Jordan and Zvelebil, 2009). However, the usage of clay for the production of containers is a relatively late phenomenon and appears after 20,000 cal BP.

V. Gordon Childe described pottery as the first deliberate use of a chemical transformation by humankind (Childe, 1951). Three different scenarios for the idea that started the invention of pottery have been proposed. It could have been analogous to bread-making or the processing of nuts (Amiran, 1965), to clay-lined storage pits that were fired because of proximity to a hearth (Bar-Yosef and Valla, 1991), or to clay linings of baskets (Mills and Crown, 1995). The shape and surface decoration of very early pottery is in fact often decorated in a way that resembles baskets (Jordan and Zvelebil, 2009).

Pottery makes it possible to prepare food over direct heat. An older cooking method like boiling in the pots which are warmed by hot stones makes it more difficult to consume the nutrients that leach into the water. During roasting, meat juice and lipids would be lost to the fire (Jordan and Zvelebil, 2009). Cooking in pottery is thus a very efficient cooking method and the nutrients that leach out of the cooked food are preserved in the liquid that can be consumed as well. Pottery can be especially useful in the preparation of plant foods. The hunted animal species in temperate and warmer climate zones do not contain enough fat to protect the human consumers from protein poisoning, the famous “rabbit starvation” (Bilsborough and Mann, 2006). Therefore, fat and starch/carbohydrates from other sources, i.e. fish or plants, must complement the diet. Many plants are indigestible or even toxic when eaten raw, and also the uptake of proteins from food is improved when the food is cooked. Furthermore, lipids could easily be rendered from fish when cooking in pottery (Jordan and Zvelebil, 2009). With pottery, palm oil extraction and the production of weaning foods is facilitated, and the food values of plants such as maize, manioc and beans are improved. Furthermore, surplus fruits can be fermented into beverages (Hoopes, 1995; Hoopes and Barnett, 1995). Pottery thus provides the opportunity of collection, storage and preparation of food and drink for feasts, and offered in this way a social advantage besides the nutritional advantage (Hoopes, 1995).

In western Europe, it had been assumed that all aspects of the Neolithisation came in a tightly bundled “Neolithic package”. It was soon realized that phenomena like farming and pottery not necessarily were connected. Farming could antedate the introduction of pottery, and vice versa (Clark, 1953). However, it was still assumed that different groups just adapted different techniques from the Neolithic package at different times. This notion has changed in the recent decades when radiocarbon dating showed that pottery had been invented millennia before agriculture.

In conclusion, pottery is beneficial for nutrition, and independent of other cultural phenomena like farming. Why was it invented at the Pleistocene-
Holocene transition, and not already much earlier?

One precondition for the invention of pottery is that the climate, as well as the mobility pattern of the people, have to be suitable for drying and firing the ceramics. This implies the presence of large enough quantities of firewood, but also predictable periods of dry weather and reduced mobility so the pots could dry several days to a few weeks before firing. Firing is the most difficult and energy-demanding stage in pottery production, but it becomes cheaper the more pots are fired at the same time. In a technique like basketry, in contrast, the effort increases linearly with the number of containers. Pottery is thus favoured in groups with a high demand for containers, i.e. larger groups, or populations that depend on the collection of small food items instead of e.g. hunting large animals (Jordan and Zvelebil, 2009).

With the beginning of the Holocene, several large mammal species became extinct in Eurasia, while rising sea levels resulted in a variety of estuarine and coastal environments. These provided predictable and varied resources, which in many cases had different seasonal availability. This favoured a new settlement pattern with semi-permanent settlements in the most productive places and smaller specialized hunting sites. The opportunity for pottery production was thus given (Clark, 1983). But also the demand for pottery increased due to e.g. shellfish collection or the hunting of marine mammals whose fat could be processed and stored in the ceramic containers. Pottery production has also been reported from other hunter-fisher-gatherer sites in similar environments. In southern Pacific Mesoamerica, for example, settlements in estuaries and mangroves were characterised by pottery, settling of permanent villages, shell middens and initial adoption of agriculture (Arroyo, 1995).

The earliest pottery is from the Late Pleistocene, but its numbers are limited. Only with the onset of the Holocene, ceramic technology increased in importance in the early centres, and spread rapidly throughout Eurasia (Jordan and Zvelebil, 2009). Besides its usefulness for food preparation and storage, it also “…provided a medium peculiarly well adapted to a variety of modelling and ornamentation” (Clark, 1979). In prehistoric societies, pottery was thus used to express group identity. As a variety of pottery designs may fulfill the same purpose, pottery is more sensitive to change than other artefacts (Becker, 1948). To present-day archaeologists, it is therefore a means to distinguish cultural groups and follow communication routes as well as developments in time. Furthermore, pottery is abundant on archaeological sites: “Its brittleness guarantees frequent breakage and disposal; its crystalline structure virtually guarantees preservation” (Braun, 1983).

5.3.2 Early centres for the invention of pottery

Three independent centres for the invention of pottery have been identified; Southern China, Japan and the Russian Far East. However, a single centre in China has also been proposed (Jordan and Zvelebil, 2009). The earliest pottery was produced by Pleistocene hunter-gatherers, before the onset of the Holocene.

China

The oldest pottery in China was recently dated to 19-20,000 BP by radiocarbon dates on the context (Wu et al., 2012). This early date makes it the oldest known pottery in the world. It was possibly invented in order to extract more nutrients/calories from the food (Shelach, 2012). Before that, the earliest pottery from southern China had been dated to 17,000-14,700 cal BP. It was stroke- and cord-marked, round-based and quartz-tempered (Jordan and Zvelebil, 2009).

In northern China, in contrast, flat-based pottery appears later than the earliest pottery of southern China, Japan and the Russian Far East.

The end of the Chinese Palaeolithic is characterised by population growth, increasing sedentari-ness, greater reliance on fishing and intensive shellfish collection. The first aspects of Neolithic economy appear in 7500 BC (9500 cal BP) with the domestication of wild rice.

Japan

In Japan, the “Jomon period” began at the end of the last glacial period. Innovations at the beginning of the Jomon period were archery and domestication of the dog. The Jomon economy included a wide range of terrestrial, marine and littoral species, for example birds, sea mammals and shellfish. Also Jomon kitchen middens are present. As the present sea level is 3–6 m lower as in 8000-7000 cal BP (6000-5000 BC), many shell middens across the former shoreline are now located up to 60 km inland. The Jomon period ended around 3000-2400 cal BP (1000-400 BC) with the arrival of rice agriculture (Roberts, 1998; Kobayashi, 2004).

Jomon pottery is decorated with cord-marks. The Incipient Jomon pottery occurs in two forms, bullet-shaped deep pots with round bases and square pots with flat bases (Kobayashi, 2004). The pottery was
5.3. THE HUNTER-GATHERER POTTERY TRAJECTORY

apparently used for cooking food, as carbonised re-
mains and signs of secondary firing were found on
assumes that the pottery was important for cooking
plant food that could not be eaten raw, thus facilita-
ting the development of the Jomon culture’s increas-
ingly sedentary lifestyle. Cooking in pots facilitated
the consumption of two of the basic Jomon aliments:
shellfish, that can be opened easily after cooking, and
acorns, that have to be boiled for an extended period
to be edible (Kobayashi, 2004).

Jomon pottery was an early example of the fact
that pottery and agriculture are completely unre-
lated: “Although the high radiocarbon dates from
the early ceramic levels of Japanese middens were at
first received with incredulity, their consistency with
the internal development of Jomon pottery has since
brought widespread acceptance and with this the re-
jection of the doctrine, prevalent since the time of
Lubbock, that the making of pottery appeared at the
same ‘stage’ as farming economy.” (Clark, 1980)

Until the middle of the 1990s, Jomon pottery was
assumed to be the oldest in the world, dated to 12,700
uncal BP (Aikens, 1995), which is around 13,000 cal
BC when calibrated with OxCal 4.0 and IntCal04
(Bronk Ramsey, 2009; Reimer et al., 2004). More re-
cently, it was dated to 16,000-10,000 cal BP (14,000-
8000 BC Kaner, 2009).

Russian far east

At the lower reaches of the Amur river in the
Russian Far East, artefacts and subsistence change
at the Late Pleistocene–Early Holocene transition.
Ground stone tools were introduced, and fishing be-
gin to play an important role. In the most favourable
zones, salmon fishing facilitated sedentariness, or
semi-sedentariness. The pottery can be decorated
with comb marks, zigzag lines, and cord impressions.
Flat bases as well as pointed bases occur (Kuzmin,
2002, 2006). The earliest pottery is dated by ther-
moluminescence and radiocarbon dating of temper
and associated charcoal to 16,000-12,300 cal BP (Zhushchikhovskaya, 2009; Dere-
vianko et al., 2004).

5.3.3 Hunter-gatherer pottery outside
Eurasia

In a global perspective, pottery among hunter-ga-
therer cultures is a wide-spread and diversified phe-
nomenon. Here, I will give two other examples for
early pottery in different regions. They are signifi-
cantly younger than the pottery from the three in-
novation centres described above, but most probable
independent inventions.

The oldest pottery on the Western Hemisphere was
found at a shell-midden site in Amazonia. It is dated
to 8-7000 cal BP (6-5000 BC) and belonged to a semi-
sedentary culture whose economy was largely based
on fishing and shellfish collection (Roosevelt et al.,
1991; Roosevelt, 1995).

Another center for the independent invention of
pottery is the southern Sahara and the Sahel region.
It was invented in the mid-tenth to early ninth mil-
leum uncal BP and produced by groups “…who
ranged from (at most) semi-sedentary to highly mo-
 bile and whose subsistence was based almost entirely
upon wild species” (Close, 1995). Not surprisingly,
the quantities of pottery use increased with decreasing
mobility of the groups.

In Northern Africa, pottery was invented in 10,000
cal BP (8000 BC); this may have been a local inno-
avation as well (Jordan and Zvelebil, 2009).

5.3.4 Spread of pottery among Eurasian
hunter-gatherers

The spread of pottery throughout Eurasia is summa-
rized by Jordan and Zvelebil (2009):

After ca. 7,500 BC (9,500 BP), in the con-
text of early post-glacial environmental con-
ditions, pottery is dispersed further to the
northwest, via the northerly route through
central Russia, the Upper Volga, into Kare-
lia and beyond, forming various local tradit-
ions of pointed-based pitted and combed
wares, such as the Sperrings pottery of
Finland, and entering the East Baltic and
northern Scandinavia by about 5,000 BC…

Additionally, a more southern route of dispersal is
possible. It might have been responsible for the in-
roduction of pottery into the farming communities
of the Near East (Jordan and Zvelebil, 2009).

In the following, I will present the earliest pottery
dates of Eurasia.

In Siberia, pottery occurred between 13,800 and
12,500 cal BP (11,800-10,500 BC McKenzie, 2009;
Kuzmin, 2002).

Ground stone tools and pottery mark the begin-
ing of the local “Neolithic” in Korea in 8000 uncal
BC, possibly even earlier (Cho and Ko, 2009).

In the Ural mountains and the Western Siberian
Plain, different pottery forms occur around 8000 cal
BP (6000 BC), these are vessels with decorations on
the whole outer surface, round or slightly pointed bot-
toms or flat bottoms. Boat-shaped vessels have also
been found. Some of the potsherds had food crusts (Chairkina and Lubov', 2009).

The oldest pottery from Western Asia differs from other early hunter-gatherer ceramics in the way it was used: Deep jars served as storage containers, while shallow dishes were used for serving. This pottery is dated to about 8000 BP (6000 BC Moore, 1995).

Pottery occurred as early as 8300 BC in the steppe regions of Russia and the Ukraine (Bailey, 2008). The technique of ceramic production spread from this region in the second half of the sixth millennium BC to the west and north, leading to the development of the pottery types Narva, Ka I:1/Sperrings and Säräisniemi 1 in Karelia (Piezonka, 2008; German, 2009). In Finland, seal hunting replaced terrestrial hunting at approximately the same time when pottery was introduced, probably because pottery was well-suited for rendering seal fat.

The Narva culture pottery forms were large pots with pointed or round bases and smaller oval bowls, possibly lamps. Most of this pottery is decorated. The conclusion after 16 $^{14}$C datings of Narva, Ka I:1/Sperrings and Säräisniemi 1 pottery is presented in table 5.3. Figure 5.5 from Hallgren (2004) illustrates many of these pottery styles.

Pottery occurs around 5500 BC (7500 cal BP) in the Baltic (Bailey, 2008; Piezonka, 2008). We have thus been able to follow the spread of pottery from three innovation centres in China, Japan and the Russian Far East towards the west, covering a timespan of more than 10,000 years. Figure 5.6 illustrates this development. Between 5000 and 4000 BC (7000-6000 cal BP), pottery is a widespread phenomenon also among northeastern to northwestern European hunter-gatherers. The radiocarbon dates for this pottery are very similar, and many age ranges overlap. Furthermore, I am not aware of corrections for freshwater- or marine reservoir effects. I am therefore not able to resolve the development of pottery in Northern Europe and cannot explain in detail how this innovation spread through the region. This emphasizes the need for studies like the one presented in chapter 6, where the oldest pottery in a region is attempted to be dated accurately by identifying reservoir effects. With accurate, i.e. reservoir-corrected, and precise datings of Northern European pottery, the spread of this innovation could be recorded and communication networks could be mapped.

However, as this is not possible yet, I have collected dates and references as well as description of the ceramics in table 5.4, without trying to sort them chronologically. Interestingly, the vessel shapes seem to be very similar throughout Northern Europe. Especially the pointed base is a recurrent trait, so it can be assumed to have functional advantages.
<table>
<thead>
<tr>
<th>Millennium cal. BC</th>
<th>Culture and/or site where pottery was found</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.</td>
<td>at the lower reaches of the rivers Wolga and Don</td>
</tr>
<tr>
<td>end of 7.</td>
<td>in the forest zone in central Russia at the upper Wolga (Upper Wolga Culture) and further to the west in the basin of the western Dvina (Serteja-group)</td>
</tr>
<tr>
<td>during 6.</td>
<td>pottery spreads to most regions of the forest steppes and forests of eastern Europe</td>
</tr>
<tr>
<td>mid 6.</td>
<td>Neman culture, southeast Baltic, pottery similar to EBK</td>
</tr>
<tr>
<td>mid 6.</td>
<td>Narva culture, eastern Baltic</td>
</tr>
<tr>
<td>6. (2. half)</td>
<td>northern forests of Karelia and Fennoscandia</td>
</tr>
</tbody>
</table>

Table 5.3: The spread of pottery through Eastern Europe and the Baltic region
Figure 5.5: Baltic ceramics. From Hallgren (2004), page 125. M – Måladalen, Å – Åland archipelago, 1 – Early Older Comb Ware pottery, 2 – Säräisiemi pottery, 3 – Narva pottery, 4 – Neman pottery, 5 – Ertebølle pottery, 6 – Linear Band pottery.
Figure 5.6: The spread of hunter-gatherer pottery through Eurasia. The gray arrow indicates the approximate time and space of the appearance of pottery. On the time axis, a climate proxy, $\delta^{18}$O values from the NGRIP ice core, is given (Rasmussen et al., 2006). High $\delta^{18}$O indicate warmer, low $\delta^{18}$O values colder climate. The end of the Glacial Period, and the beginning, can easily be seen as a significant increase in $\delta^{18}$O values. Dates of pottery are from the references mentioned in the text. Sources for illustrations of pottery: Wu et al. (2012); Kuzmin (2002); Cho and Ko (2009); the photograph of the Jomon vessel is in the public domain, the Bug-Dniester Culture vessel is from The National Museum of Archaeology and History of Moldova, http://www.nationalmuseum.md/en/timetape/5000_dc_a_doua_jumatate_a_mil_vi/neolithic_age, and the pointed-based vessel is by E. Koch, from https://sites.google.com/site/earlypotteryresearch/KochEBK.jpg.
Table 5.4: Examples for hunter-gatherer pottery in Northern Europe. Some authors define the beginning of the Neolithic as the beginning of pottery production, not as the beginning of agriculture. The cultures characterised as “Neolithic” in this table were also hunter-gatherer cultures. Where only $^{14}$C ages BP were given, I calibrated them with OxCal 4.1, using the calibration curve IntCal09, and put the 95.4% age ranges in brackets.

<table>
<thead>
<tr>
<th>Site(s)</th>
<th>Region</th>
<th>Culture/Group</th>
<th>Age/Period</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hude I am Dümmer</td>
<td>(NW Germany)</td>
<td>Rössen/ TRB</td>
<td>4200-3700 BC (uncalibrated)</td>
<td>“large vessels with pointed bases, very similar to those of the Ertebølle/Ellerbek culture of the Baltic area”</td>
<td>Bogucki, 1988</td>
</tr>
<tr>
<td>Osa</td>
<td>(Latvia)</td>
<td>“Early Neolithic”</td>
<td>5730±50 BP, 5580±80 BP and 5780±70 BP (4692-4460 BC, 4608-4262 BC and 4788-4464 BC)</td>
<td>“…large, thick-walled pots with pointed bottoms and […] small, ovoid “lamps”. The pottery is ornamented with comb stamps, lines and small pits, forming horizontal or diagonal rows or zig-zag patterns.”</td>
<td>Dolukhanov and Liiva, 1979</td>
</tr>
<tr>
<td>Sarnate</td>
<td>(Latvia)</td>
<td></td>
<td>4045-2496 BC (my calibration; extremes of 94.5% ranges from 5 datings)</td>
<td>“conical vessels with straight or S-shaped rims and small ‘lamps’”</td>
<td>Dolukhanov and Liiva, 1979</td>
</tr>
<tr>
<td>Aland</td>
<td>Early Older Comb Ware Culture</td>
<td></td>
<td>around 5000 BC; pottery from the same culture in Finland and Karelia, Russia: 5400-4200 BC</td>
<td>“un-profiled pots with a round or pointed bottom”, tempered with crushed rock, sometimes with sand, surface often decorated (cords, stamps)</td>
<td>Hallgren, 2004</td>
</tr>
<tr>
<td>Eastern Baltic</td>
<td>Narva Culture</td>
<td></td>
<td>“…it should be safe to conclude that pottery appears around 5500-5200 cal BC in the Narva Culture.”</td>
<td>“large pots with pointed base and low plates, very reminiscent of the Ertebølle clay lamps…” “The richly decorated Ertebølle vessels display clear similarities to Narva pottery…”</td>
<td>Hallgren, 2004</td>
</tr>
</tbody>
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<thead>
<tr>
<th>Site(s)/ Region</th>
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<th>Age/ Period</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE Poland, S Lithuania, SW Byelorus-sia</td>
<td>Neman Culture</td>
<td>Neman datings from Poland: 5900±100 BP, 5700±120 BP (5630-4529 BC, 4827-4335 BC); from Lithuania: 6550, 6020, 5980, 5950, 5360, all ±70 BP (the oldest: 5623-5374 BC)</td>
<td>vessels have slightly profiled shape and pointed bottoms</td>
<td>Hallgren, 2004</td>
</tr>
<tr>
<td>Melsele-Hof ten Damme (NW Belgium)</td>
<td>Rhine-Meuse-Schelde Culture</td>
<td>Mesolithic, although remains from domesticated cattle and pigs were found</td>
<td>“The potsherds are tempered with schamotte, bone and quartz and show pointed base vessels and sparse decoration”</td>
<td>Heinen, 2006</td>
</tr>
<tr>
<td>W Europe, Baltic</td>
<td>Mesolithic</td>
<td>6300-5300 BP (cal. 95.4% age range of 5800±500 BP: 6909-4621 BC)</td>
<td>pointed-based pottery is a characteristic trait of a range of subneolithic and mesolithic cultures along the whole of the Atlantic fringe and further to the east in the Baltic</td>
<td>Klassen, 2002</td>
</tr>
<tr>
<td>Dabki, Baltic coast of Pommerania</td>
<td>6300-5300 BP (cal. 95.4% age range of 5800±500 BP: 6909-4621 BC)</td>
<td>“…Mesolithic flints, rich pottery collection of Ertebølle type with an admixture of Linear Ceramic pottery, […] and especially a growing number of bones from cattle and pigs.” the pottery also indicates contacts to the East Baltic Area, e.g. Narva culture</td>
<td>Kobliszewicz, 2006; Ilkiewicz, 1991, 1997</td>
<td></td>
</tr>
<tr>
<td>Swifter-bant, Netherlands</td>
<td>Early Neolithic</td>
<td>around 3300 BC</td>
<td>“…pottery in a Nordic (Ertebølle) style and (trade) relationships with late Rössen communities…”</td>
<td>Louwe-Kooijmans, 1980</td>
</tr>
<tr>
<td>Polderweg, Netherlands</td>
<td>4700 BC</td>
<td>“Op de site Polderweg werd alleen in het hoogste niveau (4700 v. Chr.) een beperkt aantal aardewerkscherven gevonden, waaronder een karakteristiek dikwandig kommetje met puntbodem.”</td>
<td>Louwe-Kooijmans, 1998</td>
<td></td>
</tr>
<tr>
<td>Swifter-bant S2 and S3, Netherlands</td>
<td>Early Neolithic</td>
<td>3400-3200 BC, “The C14 dates correspond to the initial phases of the Michelsberg culture (Germany, Belgium) and the end of the Ertebølle culture (Denmark, Northern Germany)”</td>
<td>“…pots with a flowing S-shaped profile and round or pointed bases”</td>
<td>de Roever, 1979</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
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<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doel</td>
<td>Final (Swifter-bant)</td>
<td>Mesolithic</td>
<td>food crust 4900-1700 BC, carbonised plant/bone: 4500-4000 BC</td>
<td>“...dominated by slightly S-shaped vessels, provided with a rounded or pointed base”</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sergant et al., 2006</td>
</tr>
<tr>
<td>Finland</td>
<td></td>
<td>5300 BC</td>
<td>pottery with pointed bases; according to lipid analysis, it was used for fermentation or cooking</td>
<td>Pesonen and Leskinen, 2009</td>
</tr>
<tr>
<td>Estonian coast</td>
<td>Mesolithic</td>
<td>between 4700 and 3500 BC</td>
<td>pottery with conical bases; seal-hunter culture</td>
<td>Jaanits, 1995</td>
</tr>
<tr>
<td>Sweden</td>
<td>Ertebølle</td>
<td>4500 BC (in Northern Sweden: Early Comb Ware, slightly earlier)</td>
<td></td>
<td>Stilborg and Holm, 2009</td>
</tr>
</tbody>
</table>
Czerniak and Kabaciński (1997) propose that the term “Ertebølle” should be used for all those groups that are now called Ertebølle, Ellerbek, Lietzow, Swifterbant, Tanowo, and Dabki because of

- similar Neolithisation history, on the northern border of the Danubian colonisation, later transformation to TRB
- located (relatively) close to each other
- the pottery is technologically and stylistically quite uniform (cf. Table 5.4), even if flint technology may differ

### 5.3.5 Early farming communities

The Near East is probably the oldest center for agriculture (Roberts, 1998); here, a pre-pottery Neolithic has been identified from 12,000 to 9300 cal BP where agriculture developed from a start with experimental agriculture inside a broad-spectrum economy towards a full farming society (Roberts, 1998). Pottery was adapted in the Near East about 1000 years after the invention of farming. From then on, the “Neolithic package” was completed and spread across Europe, primarily north-westwards along the Danube-Rhine axis (Roberts, 1998). It was highly successful, partly because of its composition of domesticated species: Cattle, sheep, goats and pigs feed on different plants, and the latter can also live on human food refuse and woodland resources. The domesticated plant species in the “Neolithic package” were a good combination as well. Cereals provided energy, while pulse species could fix nitrogen and provided protein (Jarman et al., 1982).

During the last 6000 years, there has been intensive agriculture on the loess areas plains of central Europe (Bogucki, 1988). These areas had been thinly inhabited by hunter-gatherers as the natural productivity of loess habitats is low. This region provided a habitat for the first agricultural and ceramic culture in central Europe, the Linear Pottery Culture (LBK), which had originated from Danubian cultures. Contacts of the LBK with hunter-gatherer groups are documented in e.g. Belgium, where contacts with the Swifterbant culture were demonstrated, and at the site Dabki in Poland (Hauzeur, 2006; Crombé et al., 2000; Ilkiewicz, 1997). The LBK was also contemporaneous with large periods of the Ertebølle culture. In addition, two other central European cultures, Late Lengyel and Rössen culture, have been proposed as possible Neolithic trade partners of the Ertebølle culture (Fischer, 1982; Czerniak and Kabaciński, 1997).

However, the Swifterbant economy may also be classified as Neolithic. In the Rhine-Maas delta, incipient agriculture is found in the Swifterbant culture. Beyond agriculture, the material culture is very similar to the Ertebølle culture or the hunter-gatherer settlements on the lake Dümmer (see below), especially the pointed-based pottery (de Roever, 1979; Crombé et al., 2008; de Rovere, 2004; Verhart, 2003; Bogucki, 1988; Louwe Kooijmans, 1993, 2003; Louwe-Kooijmans, 1980).

Hüde I at the lake Dümmer in north-western Germany might be another indicator of contact between Mesolithic and Neolithic cultures. It is a Neolithic site and contains remains from Rössen culture and Funnel Beaker culture (TRB), both of which are farming cultures. However, over 95% of the bones belonging to the TRB culture on this site are from wild animals, so Hüde is classified as a Neolithic hunting station (Steffens, 2005). Pottery from this site, dated to 4200-3700 uncal BC, is described as “large vessels with pointed bases, very similar to those of the Ertebølle/Ellerbeck culture of the Baltic area” (Bogucki, 1988). The calibrated age is between 5100 and 4500 BC (7050-6450 cal BP), after calibration with OxCal 4.1 and IntCal09.

In the western Mediterranean, pottery exchange might have played a role in accumulation strategies that led to the transition to agriculture (Barnett, 1995). This is thus another one of the regions where pottery pre-dates agriculture.

In conclusion, there are two big lines of innovations that cross in central Europe, the pottery from Eastern Asia, and the agriculture from the Near East. These form together the “Neolithic package” that spread along the Danube into Central Europe. Northern European cultures, in contrast, adopted several of these innovations at different times, from different cultures and to a varying degree. New techniques like pottery and agriculture were incorporated into the local economy when they fit in; a complete cultural transformation can not be observed. In some cases, it took millennia from the first use of pottery or the first experiments with agriculture to a “fully-neolithised” society. The favourable economic conditions in the high-productivity coastal regions of Northern Europe were certainly a reason why agriculture was introduced so hesitantly.

### 5.3.6 The Ertebølle culture and the “neolithisation” of Northern Europe

The first half of this section focuses on the last Mesolithic culture in Northern Germany and Den-
mark, the Ertebølle culture (EBK). In this region, the neolithisation was, as described above, not at all a “Neolithic revolution”. The transition from mobile hunter-fisher-gatherers to sedentary, pottery-producing farmers was gradual and step-wise, and took place within the local population (Andersen, 1973; Hartz and Schmöleke, 2006; Glykou, 2011). The transition from the mesolithic Ertebølle culture to the neolithic Funnel Beaker culture, or the neolithisation of this region, will form the second half of this section.

The Ertebølle culture is characterised by large central settlements and smaller hunting stations (Andersen, 1989). Some of the settlements had already been in use during the Kongemose culture (table 5.2 Andersen, 1990). Over 400 shell middens are recorded from the Ertebølle culture in Denmark (Bailey, 2008). The largest are several 100 m long and several m thick. However, shell middens tend to exaggerate the importance of shells in the economy because they are better preserved than e.g. animal bones. It was estimated that only 25 to 50% of the animal food was marine (Jarman et al., 1982). However, marine resources had the advantage of being easily accessible, as a result of fish or marine mammal migration patterns, or at peak nutritional value in winter and early spring (Jarman et al., 1982). The coast provided thus important resources during seasons when terrestrial resources were poor.

A number of Ertebølle burials are known, e.g. a cemetery at Vedbæk (Petersen and Meiklejohn, 2003; Petersen, 2006).

Typical artefacts in the Ertebølle culture are T-shaped antler axes and transverse arrowheads. Permanent fishing constructions are known from numerous sites and can be very large - weirs with lengths of several 100 m have been found. The construction of these structures requires substantial efforts, including forestry to obtain suitable raw material (see above). Once completed, however, these structures provide continuous supplies of fish, while the only effort is the emptying of the fish traps. Permanent fishing structures stimulate conceptions of ownership of a certain place and increase tendencies towards sedentariness.

The submerged site Tybrind Vig (today 250 m off the coast, at a water depth of 3 m) provided excellent preservation conditions and yielded numerous organic finds. These include dugout canoes, decorated paddles, textiles (made in “needle-binding”) and ropes made of willow and lime fibres (Andersen, 1997).

In the Danish Mesolithic, some changes happen around 5700 uncal. BP (Andersen, 1973), which is around 4500 cal BC after calibration with OxCal 4.1 and IntCal09 (Bronk Ramsey, 2009; Reimer et al., 2009). The formation of kitchen middens begins, and also the increase in size and duration of settlements indicates an increasing degree of sedentariness (Andersen, 1973). This coincides with the introduction of pottery which is dated to 5610-5660 uncal. BP in Jutland (Andersen, 1973; Hartz, 1996), approximately 4400-4600 cal BC after calibration with OxCal 4.1 and IntCal09 (Bronk Ramsey, 2009; Reimer et al., 2009). Later studies date the introduction of pottery to about 4700 cal BC (Andersen, 1989). A typical Ertebølle vessel is shown in figure 5.7, another example in figure 5.5. This early pottery is thick-walled with dot ornamentation (cf. Figure 5.5), which relates it to pottery from the central and northern German Stroke Ornament Pottery Culture - e.g. pointed-base pottery from Dümmen and Boberg, which would be earlier than the previously assumed influences of the Rössen culture (Andersen, 1973, and references therein). Pointed bases are characteristic for Ertebølle pottery, but regional differences in the form of the bases can be distinguished (Figure 5.8 Hulthén, 1977).
5.3. THE HUNTER-GATHERER POTTERY TRAJECTORY

One of the aspects facilitating the introduction of agriculture in the region of the Ertebølle culture was the decreased mobility with relatively stable large settlements. Reduced mobility makes storage of resources possible, which is a first step towards a delayed-return economy. Other examples of delayed-return practices in the Ertebølle culture are permanent fishing structures and coppiced hazelwoods. Decreased mobility necessitates trade to obtain resources or prestige goods that are not present in the territory of the group. Trade has even been described as the spatial analogue of storage: the “transfer of food in the dimension of space rather than time” (Jarman et al., 1982). Trade in the Ertebølle culture is exemplified by finds of Danubian shafthole axes (Fischer, 1982).

Different models for the adoption of domestication have been proposed. One is the population pressure model, where an increase in population pressure necessitates increased food production. This is most likely to happen in stressed, marginal environments. The other model is the competitive feasting model. In this scenario, domesticated foods are used for feasting, but not needed as staples to prevent starvation. This is likely to happen among complex hunter-gatherers with dense populations, semi-sedentarism and status display items such as imported artefacts (Hayden, 1995). The latter is a good description of the Ertebølle culture, and the “food for feasting” hypothesis may prove correct for the neolithisation of Denmark and Northern Germany (see also Fischer, 2002b).

There were about 700-500 years of contact between EBK and farming groups (Blankholm, 2008), before farming was introduced in Northern Germany and Denmark. Two reasons have been suggested for this time lag, summarized by Armit and Finlayson (1995): The economic investment of many hunter-gatherer groups in specialized subsistence practices might have been too high to give them up easily, or there had been an ideological opposition to agriculture. However, such a time lag is an aspect of the socioeconomic

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Figure 5.8: Pointed bases of Ertebølle pottery – regional differences. From Hulthén (1977), Fig. 19, page 139.
CHAPTER 5. NATURE AND CULTURE

competition model for the introduction of agriculture (see above and Hayden, 1995), where domesticates only were used for special occasions.

The culture following the Ertebølle culture was the Funnel Beaker culture, TRB. In early research, it has been argued that late EBK and the entire TRB had been contemporaneous (Becker, 1955). It was suggested that the TRB culture represented the immigration of a farming culture. Today, it is clear that TRB followed EBK and was a mainly independent development. At the rivers Trave, Alster, Bille and Stecknitz, settlement regions from the Ertebølle culture correspond with those of the Funnel Beaker culture – the regions probably did not lose their economic importance as fishing and hunting sites until the beginning of the Bronze Age (Schriren, 1997). The same can be observed on sites at the Baltic Coast of Schleswig-Holstein. In the early stages of the Funnel Beaker culture, the food-producing economy only contributed about 20% of the subsistence (Hoika, 1997).

The EBK and TRB pottery also indicates an autochthonous development. During the Ertebølle period, the production of pottery was constantly improved until the technological basis for the transition to funnel beaker pottery was established (Glykou, 2011).

The nutrition at the Mesolithic-Neolithic transition is apparently complicated to reconstruct. δ¹³C values of a limited number of skeletons had shown heavy dependence on marine resources during the Mesolithic, and a sharp shift of diet towards exclusively terrestrial resources during the Neolithic (e.g. Tauber, 1981; Noe-Nygaard, 1988; Richards et al., 2003b,a). Later evidence showed that the process had been more complex, including evidence for fishing in the Neolithic (e.g. Milner et al., 2004; Liden et al., 2004) and was debated extensively (e.g. Richards and Schulting, 2006; Milner et al., 2006). Newer research includes δ¹⁵N values of human bones as well and illustrates the full dietary complexity (Figure 5.9, Fischer et al., 2007). Marine food became less important with the transition to the Mesolithic. However, aquatic food, as indicated by elevated δ¹⁵N values, was still consumed regularly in the Neolithic.

Another aspect of the Mesolithic-Neolithic transition can also be observed in human skeletons. Mesolithic skeletons have pronounced muscular attachments as result of life-long physical exertion (Bennike and Alexandersen, 2002). After the neolithisation, bones and skulls generally became less sturdy and the teeth smaller (Bennike, 1993). Heavy attrition on Mesolithic teeth was replaced by more dental decay and tooth loss in the Neolithic (Bennike and Alexandersen, 2002).

5.4 Summary

The first pottery was produced during the Last Glacial Maximum in China, while large parts of Denmark still were covered by ice. The pottery made it possible for the late-glacial hunter-gatherers to optimize the amount of nutrients they could obtain from their food resources. At the end of the Pleistocene, three centres for pottery invention can be identified in southern China, Japan, and the Russian Far East. However, pottery is only used in small quantities and does not spread from these centres until the beginning of the Holocene.

After the end of the glacial period, changing climate and sea levels resulted in the formation of new habitats, offering a variety of plant food and aquatic resources and supporting semi-sedentary complex hunter-fisher-gatherer cultures. These cultures had the opportunity to produce pottery, as a result of their restricted mobility. Furthermore, many of the new resources that became available in the Holocene, such as plant food or shellfish, necessitated containers for collecting, processing and storing.

The next two chapters will shed light on two small aspects of the developments presented here. The environmental history of the Limfjord in the mid- and late Holocene will be reconstructed in chapter 7. The earliest pottery of the Ertebølle culture will be examined in chapter 6 to date it precisely and to find out what it was used for. The neolithisation of Northern Germany will be dated by dating the latest EBK pottery and the earliest funnel beakers from a site on the Baltic coast.
Figure 5.9: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values for bone collagen of Mesolithic and Neolithic humans and dogs from Denmark plotted versus time. The one-sided “error bars” represent reservoir corrections. Individuals marked by open symbols belong to the Mesolithic–Neolithic transition (5300-5050 $^{14}\text{C}$ years BP). Open signatures supplemented with an arrow represent samples where the reservoir effect is inadequately accounted for. The horizontal dashed line at $\delta^{13}\text{C} \approx -20\%_\text{o}$ indicates a limit above which there is solid indication of a non-negligible marine dietary component. Individuals somewhat below the line may also have consumed some small quantities of marine food. Based on the presently available data the individuals (adults) above the horizontal dashed line at $\delta^{15}\text{N} \approx 9.5\%_\text{o}$ must have consumed aquatic food regularly, and the same may apply to individuals below the line if substantial parts of this dietary component derived from low trophic level organisms such as shellfish. Figure, description and interpretation from Fischer et al. (2007).
Chapter 6

Freshwater reservoir effect in Northern Germany and radiocarbon dating of pottery

In this project, the freshwater reservoir effect in Northern Germany is examined in order to date the earliest pottery of that region more accurately. Pottery is one of the most important materials for prehistoric archaeology and often used to define cultures and to study cultural contacts and developments, as chapter 5 dealt with in detail. Apart from that, it was also a remarkable innovation for Terminal Mesolithic society: Boiling in vessels over direct heat made food resources available that otherwise were indigestive, while preserving all nutrients in the liquid. These nutrients would be lost with other food preparation techniques such as roasting.

Reliable dating is an important precondition for relating the archaeological sequences to a calendar time scale and for identifying the origin of pottery. Here, the presumably oldest Ertebølle pottery from Schleswig-Holstein will be dated, i.e. the transition from the aceramic Ertebølle culture to the ceramic Ertebølle culture. Also the transition from the Ertebølle culture to the Funnel Beaker culture will be dated. This study thus attempts to date both the oldest and the youngest pottery of the Ertebølle culture.

The inducement for this study was the radiocarbon dating of food crusts from Stone Age pottery in Northern Germany. The pottery belonged to the Ertebølle culture, a hunter-fisher-gatherer (hfg) culture which existed in Southern Scandinavia, Northern Germany and Poland in the fifth millennium BC. This culture was the first in the region to produce pottery. For finding out where this innovation came from, we need to know which other cultural groups were contemporaneous with the first pottery of the Ertebølle culture. Due to the unclear stratigraphy of many of the interesting sites, a direct dating of the pottery is necessary, as there often are no associated terrestrial materials available. Fortunately, many sherds have food crusts – charred food remains on the inner side of cooking vessels which most probably formed when food scorched during preparation. These can be used for radiocarbon dating. The pottery from two inland sites, Kayhude and Schlamersdorf, in Northern Germany was dated to 5400 cal BC and 5200 cal BC, respectively – up to thousand years older than pottery from coastal sites of the same culture, less than 100 km away (Figure 6.1). Were people from inland sites so much more innovative than their fellows at the coast? Terminal Mesolithic Ertebølle inland sites in Schleswig-Holstein are often situated next to rivers. Fish bones are frequently found in the excavations, so freshwater resources must have played an important role in the Ertebølle subsistence pattern. Food crusts on pottery from these sites likely contain remains of freshwater fish, and may thus be affected by a freshwater reservoir effect. The two inland sites, Kayhude and Schlamersdorf, were close to rivers with hard water, the Alster and the Trave (Figure 6.2). Hard water contains considerable amounts of dissolved carbonate minerals which have infinitely high radiocarbon ages. A freshwater reservoir effect was therefore suspected as an alternative explanation for the high ages. The freshwater reservoir effect is a well-known phenomenon in e.g. aquatic plants (see section 2.1.4), and was also found in food crusts on prehistoric pottery (Fischer and Heinemeier, 2003). However, some skeptics still had to be convinced that a freshwater reservoir effect is a real, and not only theoretical, problem when dating food crusts on pottery (Hart and Lovis, 2007). Apparently, the number of dated samples in the study by Fischer and Heinemeier (2003) was small enough to explain the age difference between terrestrial and freshwater samples.
with statistical methods so that the hardwater effect was not necessary as an explanation. Instead of a real radiocarbon age difference, Hart and Lovis (2007) explain the measured values with a single outlier and statistical variations. The methodological weakness of that study, however, was the fact that calibrated ages were compared, thus introducing a larger uncertainty from the calibration.

The food crusts found at inland sites in Schleswig-Holstein are quite thin and homogeneous. It is thus not possible to deduce the type of food that formed the crust by just looking at it: Terrestrial (plants, meat) and aqueous food (fish, molluscs) can not be distinguished. For assessing the possibility of a freshwater reservoir effect, other methods for food crust analysis must be used. In this study, the main focus is on stable isotope (C, N) analysis, but other methods have also been tried, including petrographic microscopy, FTIR spectroscopy and lipid analysis. As an additional benefit, past dietary habits (or, more precisely, culinary practices) can be inferred when analysing the food crusts.

The problem of a possible freshwater reservoir lead to a broadly conceived study of, on the one hand, the freshwater reservoir effect in the rivers Alster and Trave, and on the other hand, of radiocarbon dating and stable isotope analysis of prehistoric pottery. For characterising the freshwater reservoir effect, its magnitude and variability, in the two rivers, water samples as well as modern plants and animals have been radiocarbon dated. For proving that ingredients with a certain reservoir age cause food crusts on pottery to have the same reservoir age, experiments with copies of Stone Age pottery were conducted. Furthermore, stable isotope measurements on experimental food crusts are used as a basis for interpreting stable isotope measurements on archaeological food crusts.

In the case of the coastal site Neustadt, not the oldest, but the youngest Ertebølle pottery will be dated. Additionally, some radiocarbon dates on pottery of
6.1 Locations

The archaeological sites Schlamersdorf, Neustadt and Kayhude as well as the rivers Alster and Trave are located in Germany’s northernmost federal state, Schleswig-Holstein. The Trave is the biggest river of Schleswig-Holstein that flows into the Baltic sea (Schleswig-Holstein’s ministry of environment and agriculture 2003, Ostholstein und Lübeck). The Alster drains into the Elbe in Hamburg. The rivers run through a morainal landscape from the last two Ice Ages. The Trave only passes upper moraines (from the Saale glaciation). The pedogenic bedrock in the between upper and lower moraines (the latter from the Weichselian glaciation), whereas the Alster runs through a morainal landscape from the last two Ice Ages. The Trave only passes upper moraines (from the Saale glaciation), whereas the Alster runs through a morainal landscape from the last two Ice Ages. The Trave only passes upper moraines (from the Saale glaciation), whereas the Alster runs through a morainal landscape from the last two Ice Ages. The Trave only passes upper moraines (from the Saale glaciation). The pedogenic bedrock in the upper moraines is glacial till, Geschiebesand, with about 20% calcium carbonate. The glacial sand in the lower moraines, Geschiebemergel, only contains 0–5% calcium carbonate (Stewig, 1982, and references therein).

The two inland sites regarded here were shortly occupied hunting sites from the Ertebølle culture. A short occupation time of a settlement site can be derived from different findings, including the presence of flint artefacts while there is no indication for flint knapping or the absence of pollen of settlement indicators like ribwort plantain or sorrel.

The site at Schlamersdorf lies about 7 km north west of Bad Oldesloe in the valley of the river Trave, in a valley section which is 2 km long and 700 m wide and narrows to the North and South to 200 m. The site regarded here is officially called Schlamersdorf LA 5, as another site, Schlamersdorf LA 15, is nearby. In the following, Schlamersdorf LA 5 will only be called Schlamersdorf. The site is situated on a low spit of land that reached into the former lake or river system. During the Atlantic period, there was a large body of water in the Trave valley with a slow current. Probably the Trave already ran through this lake system during the Boreal (Cimiotti, 1983). In the Atlantic, a strong aggradation of the lake basin started that lead to a lowland with fens through which the river Trave was flowing, surrounded by wetlands. Through the dry phase of the Sub-Boreal, the level of water sank and forests spread along the river, resulting in the formation of peat (“Bruchwaldtorf”) but are drowned again during the cool and humid Sub-Atlantic, leading to fens and the formation of fen peat. Today, the Trave valley would still be dominated by fens if there had not been anthropogenic changes such as straightening of the river, drainage and pasturing (Cimiotti, 1983).

Already in the 1930s, stone age artefacts were found 3 km northwest of Schlamersdorf when the Trave was straightened on a stretch of 350 m. The finds (different antler and flint artefacts and potsherds) belonged to the Ertebølle culture. In 1985, K. Bokelman and S. Hartz tried to find the settlement site where these finds came from, and in 1986-1989, a total area of 400 m² was excavated, not only for reconstructing the situation at the settlement, but also for reconstructing the development of the lake/river which now is the Trave (Hartz, 1997). At Schlamersdorf, there are two sites called LA5 and LA15 (LA as abbreviation of “Landesaufnahme”) which were excavated in 1986-1990 in the course of the project “Neolithisation in Schleswig-Holstein” of the DFG (Deutsche Forschungsgemeinschaft, German Research Association). About 3500 flint artefacts were excavated, furthermore 800 potsherds, 400 unworked bones and antler fragments, three antler tools, one sandstone axe, numerous pot boilers and pieces of burnt flint and some wooden stakes that had been rammed into the lake/river ground (Hartz, 1996). In spite of the large number of flint tools, there is no evidence for the production of them (Heinrich, 1993). This supports the interpretation of Schlamersdorf as being a specialized hunting or fishing station.

A detailed zoological analysis is available for the bones found at Schlamersdorf (Heinrich, 1993). In summery, the fish bone assemblage is dominated by Northern pike (Esox lucius). Other important fish are cyprinids (Cyprinidae) and European perch (Perca fluviatilis) The comparatively high number of cyprinids is consistent with their availability in the river. Also the Northern pike has been important for prehistoric fishing in middle and northern Europe, although it can be expected that it is overrepresented in the archaeological record because of the high resistance of its bones (Heinrich, 1993). The same effect can be expected for perch bones, because they are also more resistant than some other bones. Es-
especially the very small ones could be taphocoenotic. There were bones from at least 11 individuals of waterfowl and 1 wild boar, 2 red deer and one aurochs that probably had been hunted for meat. Some smaller mammals like wildcat, European otter, European beaver and red squirrel may have been hunted for their fur. A large number of different mice can best be explained with the ideal life conditions for these species in the surroundings of the site Heinrich (1993). Schlammersdorf has been dated by different methods. Pollen analysis dates the site to the Atlantic before the elm decline. Radiocarbon calibration of the pollen profile assigns an age of 5400±27 to the EBK find layer (Hartz, 1993b).

Kayhude is situated 15 km north of Hamburg next to the river Alster. The site is situated in a narrow flood plain (about 50 m wide) with geest ridges on both sides of the Alster. North of the site there is the fen “Wakendorfer Moor”, to the south the “Niendorfer Moor”. Both fens are likely to be former lakes. During river regulation works, numerous organic finds were dug up from the fluvial sediments. The site was characterized by a lot of mesolithic surface finds (Clausen, 2007). It was excavated in 2005/2006 by Schleswig-Holstein’s state office for archaeology (“Archäologisches Landesamt”) on an area of 80 m². 1500 finds could be excavated, among them about 70 were potsherds. All find material came from the waste zone in open water. Pollen analysis showed that the site was in a shallow water region which slowly sedimented. The Alster at that time was about 50 m wide and often changed its riverbed (pers. comment Ingo Clausen 2007). A 8 m long row of wooden poles with a length of up to 70 cm can be interpreted as a fish weir. According to ¹⁴C datings, it was constructed around 5000 BC. Other finds were antler axes (among them several T-axes), typical Ertebolle pottery, wooden tools, a stone mace head, pot boilers and several bone and antler remains from wild animals (Clausen, 2007). One date of a foodcrust on
a potsherd gave the age 5400 BC, which is 400 years older than the fish weir and almost 800 years older than pottery from coastal sites (Clausen, 2007).

Layers of sand and detritus were washed ashore and had influence on the finds of the upper layers. Some of the finds are positioned diagonally or upright in the sand because they had been moved by the water. It is therefore difficult to draw a stratigraphy and identify associated artefacts. Therefore, only finds from a stone layer at the bottom of all the layers were chosen for this study. The stone layer seemed to be undisturbed and contained two T-axes, a mace head and many ceramic and flint artefacts (pers. comment Ingo Clausen 2007).

6.2 Modern samples

All modern samples were collected close to the archaeological sites of Kayhude/Alster and Schlammersdorf/Trave. Water samples from different seasons and different years illustrate the temporal variability of the reservoir effect in Alster and Trave. Samples of plants and animals from both rivers show how the effect propagates in the food web. Finally, experimental food crusts on copies of Stone Age pottery demonstrate how the reservoir age of the ingredients is reflected in the food crusts. Figure 6.2 shows a map with both rivers examined in this study. The Alster discharges into the Elbe in Hamburg, the Trave into the Baltic Sea at Lübeck/Travemünde. Both survey stations are marked by a stone layer at the bottom of all the layers were chosen for this study. The stone layer seemed to be undisturbed and contained two T-axes, a mace head and many ceramic and flint artefacts (pers. comment Ingo Clausen 2007).

6.2.1 Water

$^{14}$C, $\delta^{13}$C and $\delta^{18}$O were measured on DIC from water samples collected from each river on August 21st, 2007; September 25th, 2008; February 18th, 2009 and July 6th, 2010. The water sample collection sites (Figure 6.2) were directly at the archaeological site (Kayhude, Alster) or few km downriver (Schlammersdorf, Trave). For comparison, measurements of the concentrations of Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$ were obtained from “Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein”, formerly “Landesamt für Natur und Umwelt”. These were measured at Wulksfelde/Alster and Warderbrück/Trave, downriver of the lake Wardersee. Both survey stations are marked with black crosses on Figure 6.2. Furthermore, $^{14}$C and stable isotope results were related to precipitation measurements (Deutscher Wetterdienst, 2007-2010) at three stations, Schleswig, Fehmarn and Hamburg-Fuhlsbüttel, which are also shown on the map (Figure 6.2).

$^{14}$C, $\delta^{13}$C, $\delta^{18}$O

The results of $^{14}$C, $\delta^{13}$C and $\delta^{18}$O on water DIC are presented in table 6.1 and Figure 6.3. All water samples have $^{14}$C ages greater than 1000 $^{14}$C years (1170 to 2620 $^{14}$C-years), while $\delta^{13}$C values range between -15 and -9‰ and $\delta^{18}$O values between c. +3 and +6‰. At pH values between 7 and 9, which are typical for most aquifers, the dominant DIC species is bicarbonate, HCO$_3^-$ (Emrich et al., 1970; Romanek et al., 1992). This range of pH values is certainly a good representation of the Alster and Trave, as the pH value measured in the Wardersee, through which the Trave flows, is 8.4 to 8.9 (Nixdorf et al., 2003). During the DIC extraction, all bicarbonate is converted into CO$_2$. During this step, no fractionation takes place, as

- the reaction is complete, and all HCO$_3^-$ is converted into CO$_2$ and
- no exchange with atmospheric CO$_2$ is possible during extraction.

The DIC $\delta^{13}$C values should thus basically represent HCO$_3^-$ $\delta^{13}$C values. The $\delta^{13}$C values of Alster and Trave water DIC are inside the distribution that Keeley and Sandquist (1992) found for a collection of published water DIC values: -21.2 to +1‰. $\delta^{13}$C values in the Alster are, with the exception of September 2008, between 1.37 and 5.91‰ lower than in the Trave. Values of almost -15‰ are close to the minimum HCO$_3^-$ $\delta^{13}$C values that are expected in river water: CO$_2$ in the soil has $\delta^{13}$C values around -25‰. When this CO$_2$ is dissolved in water, e.g. rainwater or shallow groundwater, it forms carbonic acid which dissociates almost completely. At equilibrium and 10°C, the $\delta^{13}$C value of bicarbonate is about 9.5‰ higher than that of the CO$_2$ (Emrich et al., 1970; Romanek et al., 1992). The dominant DIC species in the river water, bicarbonate, has thus $\delta^{13}$C values of at least -15‰. More negative values indicate the presence of CO$_2$ in the DIC. Other DIC sources would lead to higher $\delta^{13}$C values, such as dissolved carbonate with -3 to +3‰ or atmospheric CO$_2$ with -7‰
Table 6.1: Measurements on water DIC from Alster (A) and Trave (T), collected on August 21st, 2007; September 25th, 2008; February 18th, 2009 and July 6th, 2010. The reservoir age was estimated by comparing the pmC of the DIC with the pmC of the contemporaneous atmosphere (table 6.2 and equation 2.9). Water $\delta^{18}O$ in VSMOW is calculated from DIC $\delta^{13}C$ by assuming isotopic equilibrium at 25°C (see text for discussion and calculation of water $\delta^{18}O$ values at 0°C).

<table>
<thead>
<tr>
<th>River, Date</th>
<th>SID</th>
<th>DIC pmC</th>
<th>DIC $^{14}C$</th>
<th>DIC $\delta^{13}C$ (%VPDB)</th>
<th>DIC $\delta^{18}O$ (%VPDB)</th>
<th>Water $\delta^{18}O$ VPDB</th>
<th>Res. age estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Aug 07</td>
<td>12503</td>
<td>78.30±0.30</td>
<td>1997±33</td>
<td>-14.96±0.05</td>
<td>4.41±0.07</td>
<td>-4.69±0.07</td>
<td>2418±44</td>
</tr>
<tr>
<td>A, Sep 08</td>
<td>13618</td>
<td>72.18±0.43</td>
<td>2619±48</td>
<td>-10.92±0.05</td>
<td>6.60±0.06</td>
<td>-3.05±0.06</td>
<td>3044±57</td>
</tr>
<tr>
<td>A, Feb 09</td>
<td>14621</td>
<td>82.75±0.36</td>
<td>1521±35</td>
<td>-14.85±0.05</td>
<td>2.98±0.05</td>
<td>-6.17±0.05</td>
<td>1873±41</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>15871</td>
<td>75.49±0.24</td>
<td>2259±26</td>
<td>-14.27±0.05</td>
<td>6.04±0.06</td>
<td>-3.01±0.06</td>
<td>2638±40</td>
</tr>
<tr>
<td>T, Aug 07</td>
<td>12504</td>
<td>86.45±0.57</td>
<td>1170±55</td>
<td>-13.59±0.05</td>
<td>6.09±0.05</td>
<td>-2.96±0.05</td>
<td>1622±62</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>13619</td>
<td>78.04±0.42</td>
<td>1992±44</td>
<td>-11.33±0.05</td>
<td>5.86±0.06</td>
<td>-3.20±0.06</td>
<td>2417±53</td>
</tr>
<tr>
<td>T, Feb 09</td>
<td>14623</td>
<td>86.38±0.35</td>
<td>1176±33</td>
<td>-8.94±0.05</td>
<td>4.95±0.05</td>
<td>-4.14±0.05</td>
<td>1528±45</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>15875</td>
<td>75.52±0.25</td>
<td>2255±27</td>
<td>-11.86±0.05</td>
<td>5.87±0.05</td>
<td>-3.19±0.05</td>
<td>2634±41</td>
</tr>
</tbody>
</table>

Table 6.2: Atmospheric $^{14}C$ levels, expressed as $\Delta^{14}C$, pmC and $^{14}C$ age. Monthly means are given for the months in which water samples had been collected, and averages of the growing seasons before the sampling of aquatic plants and animals (Data from Levin et al., 2010, and pers. comm. I. Levin 2012).

<table>
<thead>
<tr>
<th>Timespan</th>
<th>$\Delta^{14}C$</th>
<th>pmC</th>
<th>$^{14}C$ age</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 2007</td>
<td>50.7</td>
<td>105.80</td>
<td>-453</td>
</tr>
<tr>
<td>September 2008</td>
<td>47</td>
<td>105.44</td>
<td>-425</td>
</tr>
<tr>
<td>February 2009</td>
<td>37.3</td>
<td>104.47</td>
<td>-352</td>
</tr>
<tr>
<td>July 2010</td>
<td>40.7</td>
<td>104.83</td>
<td>-379</td>
</tr>
<tr>
<td>growing season up to August 2007</td>
<td>49.1</td>
<td>105.64</td>
<td>-440</td>
</tr>
<tr>
<td>growing season up to September 2008</td>
<td>46.5</td>
<td>105.39</td>
<td>-421</td>
</tr>
<tr>
<td>growing season before February 2009</td>
<td>46.5</td>
<td>105.39</td>
<td>-421</td>
</tr>
<tr>
<td>growing season up to July 2010</td>
<td>37.6</td>
<td>104.52</td>
<td>-355</td>
</tr>
</tbody>
</table>

Andrews et al. (1993). The lowest $\delta^{13}C$ value I measured for water DIC is -14.96%, which thus agrees with the assumption that the dominant species in the rivers I analyse is bicarbonate.

$^{14}C$ ages of water DIC are between 1170 and 2620 $^{14}C$ years. The $^{14}C$ age of Alster DIC is for every sampling date higher than that of Trave DIC (Table 6.1), although the $\delta^{13}C$ values are lower. If the only source for high ages were dissolved carbonate minerals, and the only source for low ages soil CO$_2$, then the low $\delta^{13}C$ values of the Alster are inconsistent with the high $^{14}C$ ages. A possible explanation is that the dissolved CO$_2$ in the water entering the Alster derives from the dissolution of old organic matter, like peat. Another possible explanation is the fact that the Trave flows through a lake, Wardersee, which has an average depth of 3.7 m and consists of two parts that are only connected via a 5 m wide, shallow ditch (Nixdorf et al., 2003). This leads to a comparatively long residence time of the water and facilitates exchange with atmospheric CO$_2$. $\delta^{13}C$ and $^{14}C$ age (Figure 6.4) are strongly correlated in the Alster ($r=0.82$, $R^2 = 0.67$), but not in the Trave ($r=0.11$, $R^2 = 0.01$). Without the samples from February 2009, though, the correlation coefficients are $r=0.95$, $R^2 = 0.91$ for the Alster and $r=0.89$, $R^2 = 0.79$ for the Trave (Figure 6.5). Higher $\delta^{13}C$ values indicate a higher proportion of fossil carbonates (which have $\delta^{13}C\approx0\%$), and this causes higher $^{14}C$ ages, as the fossil carbonates are $^{14}C$-free. In some cases of simple systems, the $\delta^{13}C$ values can be used to correct the $^{14}C$ age of water DIC (Boaretto et al., 1998). Their equation assumes only two sources of carbon in the water, CO$_2$ from the root zone with modern $^{14}C$ concentrations, and old dissolved carbonate minerals. Apparently, the Alster and Trave are not such simple two-component systems, as $^{14}C$ ages corrected by this equation would be between -2160 and -7085 $^{14}C$ years BP. As mentioned above, other sources of old carbon have to be taken into account, such as mineralisation of old organic matter, e.g. peat. The values from February 2009 are different from the values of the other samples, which were collected in summer and autumn. A possible reason is the winter weather in the weeks before sample collection. As the ground was frozen, rain- and meltwater could not penetrate the soil and dissolve soil CO$_2$. With a lower concentration of dissolved CO$_2$, the water is less acidic and can dissolve less carbonate. The frozen ground can thus lead to lower $^{14}C$ ages, because less old carbonate is dis-
solved, but also to higher $\delta^{13}C$ values, because less CO$_2$ from respiration in the soil enters the water. As at least some of the variability of the $^{14}C$ ages and $\delta^{13}C$ values is explained by short-term fluctuations in precipitation, it is probable that other short-term phenomena like frost in winter have a similar effect.

$\delta^{18}O$ measurements on water DIC were readily available during the $\delta^{13}C$ measurements. They will briefly be discussed here, although for a thorough discussion, $\delta^{18}O$ should have been measured directly on the water. However, $^{18}O$ in the different dissolved carbonate phases (=DIC) exchanges rapidly with the water, so that DIC $\delta^{18}O$ reflects water $\delta^{18}O$ (Clark and Fritz, 1997). Expressed as % VSMOW, the water DIC has $\delta^{18}O$ values between 33.9 and 37.1%. $^{18}O$ in the different dissolved carbonate phases (=DIC) exchanges rapidly with the water, so that DIC $\delta^{18}O$ reflects water $\delta^{18}O$ (Clark and Fritz, 1997). Expressed as % VSMOW, the water DIC has $\delta^{18}O$ values between 33.9 and 37.1% VSMOW. The DIC is extracted as CO$_2$ gas, and the fractionation factor between CO$_2$(g) and water is $10^3 \ln \alpha = 40.1$ at 25°C (Bottinga, 1968). For 0°C, the fractionation factor would be 45.67%. The water in equilibrium with this CO$_2$ would thus have $\delta^{18}O$ values between -6.2 and -3.0% VSMOW at 25°C and between -11.77 and -8.57% VSMOW at 0°C (for details on calculations of isotopic fractionation, see Clark and Fritz, 1997). These are typical values for meteoric water, see section 2.2.3. At both rivers, the lowest $\delta^{18}O$ values occurred in February 2009, while there was still lying snow. The same tendency was observed for precipitation collected in Cuxhaven (section 2.2.3).

The $\delta^{18}O$ values of the DIC in Alster and Trave are inside the range of $\delta^{18}O$ values from precipitation in Cuxhaven, but heavier than the Cuxhaven average. Evaporation, for example in lakes through which a river flows (e.g. the Wardersee in case of the Trave) or in lakes which recharge the groundwater that enters Alster and Trave, is a possible explanation.

$\delta^{18}O$ values were compared to isotope data from rivers from the GNIR database (Global Network of Isotopes in Rivers, http://www-naweb.laea.org/narp/ih/IBS_resources_gnir.html). $\delta^{18}O$ values from Alster and Trave in the range of typical values from Northern German rivers. The $\delta^{18}O$ values in Alster and Trave, measured during summer and corrected with the fractionation factor for 25°C, are greater than -4%. This is seldom in the Northern German rivers. At the mouth of the Schelde, however, values greater than -4% VSMOW are quite common (data obtained from RUG Groningen, CIO), probably due to evaporation (pers. comm. Stefan Terzer 2012). It should be kept in mind that the $\delta^{18}O$ measurements of DIC and those on water are not completely equivalent, so the $\delta^{18}O$ measurements presented here cannot be used for accurate hydrological conclusions. For that purpose, the oxygen of the water itself, and not of the DIC, should be measured. Also the assumption that summer water temperatures in the rivers are as high as 25°C is debatable, considering my experience of summer weather in Schleswig-Holstein. In future studies, $\delta^{18}O$ should be measured both directly on the water and on DIC, and be compared allowing for the actual water temperature.
Figure 6.3: Measurements on water DIC from Alster (A) and Trave (T), collected on August 21st, 2007; September 25th, 2008; February 18th, 2009 and July 6th, 2010. Scatter plots of $^{14}$C age-$\delta^{13}$C, $^{14}$C age-$\delta^{18}$O and $\delta^{13}$C-$\delta^{18}$O are shown.
Figure 6.4: Measurements on water DIC from Alster (A) and Trave (T), collected on August 21st, 2007; September 25th, 2008; February 18th, 2009 and July 6th, 2010. Correlations of $^{14}$C age-$\delta^{13}$C, $^{14}$C age-$\delta^{18}$O and $\delta^{13}$C-$\delta^{18}$O are shown. $^{14}$C, $\delta^{13}$C and $\delta^{18}$O values are listed in table 6.1.
Figure 6.5: Measurements on water DIC from Alster (A) and Trave (T), collected on August 21st, 2007; September 25th, 2008; and July 6th, 2010. Correlations of $^{14}$C age-$\delta^{13}$C, $^{14}$C age-$\delta^{18}$O and $\delta^{13}$C-$\delta^{18}$O are shown (the same correlations as in figure 6.4, but without the sample from February 2009). $^{14}$C, $\delta^{13}$C and $\delta^{18}$O values are listed in table 6.1.
Cation concentrations

In 2007, 2008 and 2010, the carbonate hardness was measured immediately after sampling with test strips (Merckoquant Carbonate Hardness Test 1. 10648. 0001, table 6.3). Carbonate hardness is the portion of alkaline earth ions present in the water for which there exists an equivalent amount of hydrogen carbonate ions and carbonate ions. Carbonate hardness is thus the concentration of \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \), in contrast to the general term water hardness which indicates the total concentration of alkaline earth ions.

pH measurements for the rivers were not available, but in the Wardersee, a pH of 8.4 was measured. The measurement was performed in April 1996, but the pH is reported to vary only slightly (Nixdorf et al., 2003), for example was the maximum value only 8.9 (in April 1997). At this pH, most of the DIC occurs in the form of bicarbonate (Olsson and Kaup, 2001). The carbonate hardness should thus be a good indicator of DIC concentration, as we can assume that almost no DIC existed in the form of \( \text{CO}_2 \). The carbonate hardness measured with the test strips is given in units of German hardness, °dH. This unit is commonly used for the general water hardness, the total concentration of equivalent cations.

For comparison, the Ca and Mg measurements for the Trave (measured downriver of the Wardersee at Warderbrück) and Alster (measured at the gauge Wulksfelde, black crosses on Figure 6.2) are given (Table 6.3). At the Alster, Ca+Mg was only measured from 1997 to 2006 and in 2011. In the following table, the average of the period 1997-2006 (pers. comm. Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2007) is given for the years 2007 and 2008. For water samples from 2009 and 2010, the average value of 2011 is given for comparison (pers. comm. Landesamt für Landwirtschaft, Umwelt und ländliche Räume des Landes Schleswig-Holstein, 2012). No measurement uncertainties were given for the Ca and Mg measurements, so I estimate it to be quite large, about 10 mg/L, which certainly overestimates the actual measurement uncertainty, but is a typical increase or decrease from one month to another. This large assumed measurement uncertainty takes the fact into account that water sample collection and Ca+Mg measurement often were not done on the same day of the month.

In the Trave, values between 66 and 122 mg Ca/L were measured during the years 2007-2011. In the Alster, 41 to 72 mg Ca/L during January-September 2011 (table 6.3). Especially in the Trave, higher values tend to occur during the winter months, lower values during the summer months (pers. comm. Landesamt für Natur und Umwelt des Landes Schleswig-Holstein, 2007).

For comparison, the carbonate alkalinity (in mg CaCO\(_3\)/L) of three British rivers was measured to 150, 200 and 245 mg/L (Keaveney and Reimer, 2012) which corresponds to Calcium ion concentrations of 60, 80 and 98 mg/L, respectively, quite similar to the values from Schleswig-Holstein. The Ca concentration should be a good indicator for the amount of bicarbonate that derives from fossil calcium carbonate dissolution. However, the Alster has lower Ca concentrations than the Trave, although it has higher DIC \(^{14}\)C ages.

In British and Irish rivers and lakes, there was a weak correlation between water alkalinity and reservoir age of fish bones: \( R^2 = 0.47 \). For lakes only, the correlation coefficient was \( R^2 = 0.68 \). Regarding only the two rivers where water samples were dated, however, the one with the lower carbonate alkalinity (river Ouse at York, 150 mg CaCO\(_3\)/L) has a higher water \(^{14}\)C age (1067±47 \(^{14}\)C years BP) than the one with the higher carbonate alkalinity (river Trent at Flixborough, 200 mg CaCO\(_3\)/L), where the water was modern (Keaveney and Reimer, 2012). This corresponds to the situation in Northern Germany. The correlation between Ca content or carbonate alkalinity and \(^{14}\)C age is apparently only visible over large ranges of alkalinitities.

As bicarbonate in the river can derive both from silicate mineral solution and carbonate solution (section 2.3, equations 2.20 and 2.21), the concentrations of cations in the water (\( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+ \)) can be used for estimating the ratio of \(^{14}\)C-free bicarbonate to total bicarbonate (Broecker and Walton, 1959):

\[
\frac{\text{\(^{14}\)C-free \text{HCO}_3^-}}{\text{total \text{HCO}_3^-}} = \frac{(\text{Ca}^{2+} + [\text{Mg}^{2+}]) - 2(\text{Na}^+ + [\text{K}^+])}{3([\text{Na}^+] + [\text{K}^+] + (\text{Ca}^{2+} + [\text{Mg}^{2+}]) - 2(\text{Na}^+ + [\text{K}^+] + \text{Ca}^{2+}))} \tag{6.1}
\]

where \([\text{Ca}^{2+}]\) etc. are the concentrations of the cations in equivalent per litre. According to this estimation and the data from Alster and Trave in 2006 (averages over the whole year), the Trave should contain 30% \(^{14}\)C-free \( \text{HCO}_3^- \) and the Alster 22%. The Alster DIC should thus be “younger”, although the opposite is the case. So, neither the Calcium concentration nor the cation ratios can predict which river has the higher DIC radiocarbon age. As mentioned above, the high ages could also be caused by the mineralisation of old organic matter.
CHAPTER 6. FRESHWATER EFFECT IN NORTHERN GERMANY

<table>
<thead>
<tr>
<th>River, Date</th>
<th>Carbonate hardness (°dH)</th>
<th>Ca + Mg (mg/l)</th>
<th>(°dH) Ca + Mg</th>
<th>Precipitation (mm, week)</th>
<th>Precipitation (mm, month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Aug 07</td>
<td>10.5 (5)</td>
<td>66.7±9.58</td>
<td>9.3±1.3</td>
<td>10 (HH)</td>
<td>134.9 (HH)</td>
</tr>
<tr>
<td>T, Aug 07</td>
<td>13 (7.5)</td>
<td>90.6±10</td>
<td>12.7±1.4</td>
<td>19.3 (SL)</td>
<td>116.8 (SL)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.1 (F)</td>
<td>103.8 (F)</td>
</tr>
<tr>
<td>A, Sep 08</td>
<td>10 (4.5)</td>
<td>66.7±9.58</td>
<td>9.3±1.3</td>
<td>1.3 (HH)</td>
<td>14 (HH)</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12 (7.5)</td>
<td>76.9±10</td>
<td>10.8±1.4</td>
<td>2.4 (SL)</td>
<td>33.9 (SL)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6 (F)</td>
<td>19.2 (F)</td>
</tr>
<tr>
<td>A, Feb 09</td>
<td>(5)</td>
<td>63.0±9.18</td>
<td>8.8±1.3</td>
<td>6.7 (HH)</td>
<td>27.1 (HH)</td>
</tr>
<tr>
<td>T, Feb 09</td>
<td>(8)</td>
<td>130.4±10</td>
<td>18.3±1.4</td>
<td>11.1 (SL)</td>
<td>34.4 (SL)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>5.8 (F)</td>
<td>24.1 (F)</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>11</td>
<td>63.0±9.18</td>
<td>8.8±1.3</td>
<td>7.10 (HH)</td>
<td>26.80 (HH)</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>10</td>
<td>81.8±10</td>
<td>11.5±1.4</td>
<td>0.20 (SL)</td>
<td>36.10 (SL)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.60 (F)</td>
<td>28.70 (F)</td>
</tr>
</tbody>
</table>

Table 6.3: Water hardness of Alster and Trave, measured with different techniques (see text). The water hardness of the first three samples was measured again in February 2010, after the samples had been stored cooled, dark and in sealed bottle. The result of this measurement are given in brackets. Precipitation data for the three stations Hamburg-Fuhlsbüttel (HH), Schleswig (SL) and Fehmarn (F) are given as accumulated amount in mm of the week or the month prior to sampling (see Figure 6.2 for a map of the stations for precipitation measurements).

Precipitation records

Daily sums (in mm) of precipitation were obtained from the German Weather Service (Deutscher Wetterdienst) for the three stations Schleswig, Fehmarn and Hamburg-Fuhlsbüttel (Deutscher Wetterdienst, 2007-2010). The total amount of precipitation in the week and in the month before sample collection was calculated. For every river, it was checked whether the amount of precipitation correlated with the $^{14}$C age or the $\delta^{13}$C values. The correlations between the measured parameters and the precipitation are shown in table 6.4. In all cases, the correlations of $^{14}$C or $\delta^{13}$C with precipitation data are negative. The more rain in the period before sampling,

1. the lower the $^{14}$C age (more “modern” carbon, relatively less CaCO$_3$)
2. the lower the $\delta^{13}$C values (more terrestrial material)

In almost all cases, the correlation of the precipitation of the week before sample collection and the $^{14}$C age is stronger than the correlation between monthly precipitation and $^{14}$C age. The only exception is the Trave and the precipitation data from HH-Fuhlsbüttel (week: $r = -0.52$, month: $r = -0.59$). This means that short-term precipitation fluctuations have a considerable influence on the $^{14}$C age of water DIC. This could explain the large variability of water DIC $^{14}$C ages from year to year / in different seasons. In the Alster, the correlation of $\delta^{13}$C with the accumulated precipitation of the week before sampling is larger than the correlation with the accumulated precipitation of the whole month. In the Trave, however, $\delta^{13}$C values are more strongly correlated with precipitation in the month before sampling, and $\delta^{18}$O values are totally uncorrelated with the weekly precipitation (table 6.4). This is probably due to the longer residence time of water in the Trave before it reaches the sampling station, which is located downriver of the Wardersee. The correlation of Trave water DIC $^{14}$C age and precipitation/week is also especially good for Schleswig and Fehmarn, so the precipitation in the north-eastern part of Schleswig-Holstein has an influence both on water level and water DIC $^{14}$C age in the Trave.

In conclusion, the $^{14}$C ages of water DIC are governed by the origin of the water, as is shown by the correlation of $^{14}$C ages and $\delta^{13}$C values. The large fluctuations of $^{14}$C age, $\delta^{13}$C and $\delta^{18}$O values are to a large extent determined by variations in local precipitation. For being certain about this, the rivers should have been sampled at shorter time intervals, e.g. weekly or monthly. Furthermore, the pH of the water samples should be measured directly and the carbonate hardness/alkalinity should be measured with more sophisticated methods than with test strips. Water samples collected in autumn, early winter and spring would complete the scheme.
6.2. MODERN SAMPLES

Table 6.4: Correlation coefficients, Pearson’s r, of $^{14}$C age and $\delta^{13}$C with the accumulated precipitation of the week and the month before sampling. HH: Hamburg-Fuhlsbüttel, SL: Schleswig, F: Fehmarn.

<table>
<thead>
<tr>
<th></th>
<th>month HH</th>
<th>month SL</th>
<th>month F</th>
<th>week HH</th>
<th>week SL</th>
<th>week F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alster $^{14}$C</td>
<td>-0.26</td>
<td>-0.18</td>
<td>-0.21</td>
<td>-0.63</td>
<td>-0.61</td>
<td>-0.65</td>
</tr>
<tr>
<td>$\delta^{14}$C</td>
<td>-0.52</td>
<td>-0.43</td>
<td>-0.49</td>
<td>-0.94</td>
<td>-0.58</td>
<td>-0.65</td>
</tr>
<tr>
<td>$\delta^{18}$O</td>
<td>-0.26</td>
<td>-0.20</td>
<td>-0.20</td>
<td>-0.45</td>
<td>-0.69</td>
<td>-0.69</td>
</tr>
<tr>
<td>Trave $^{14}$C</td>
<td>-0.59</td>
<td>-0.56</td>
<td>-0.55</td>
<td>-0.52</td>
<td>-0.92</td>
<td>-0.91</td>
</tr>
<tr>
<td>$\delta^{13}$C</td>
<td>-0.72</td>
<td>-0.76</td>
<td>-0.76</td>
<td>-0.38</td>
<td>-0.28</td>
<td>-0.29</td>
</tr>
<tr>
<td>$\delta^{18}$O</td>
<td>0.47</td>
<td>0.53</td>
<td>0.52</td>
<td>0.09</td>
<td>-0.01</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

6.2.2 Aquatic plants

Aquatic plants assimilate water DIC through photosynthesis and are expected to smooth out short-term fluctuations of water DIC $^{14}$C and $\delta^{13}$C values because they assimilate over the whole growing season. Basically, aquatic plants represent the second level of the aquatic food chain and are suggested/reported to have been used for human nutrition/as food source for Stone Age populations. For example, the rhizomes of both Nuphar and Nymphaea (see section 2.3) have been widely used as human food (Hutchinson, 1975, and references therein). Nuphar lutea is also able to metabolize anaerobically and produce alcohol, hence its common English name “brandy bottle” (Hutchinson, 1975). However, I am not aware of any evidence for the exploitation of this product of Nuphar lutea in the Stone Age.

Ten samples of aquatic plants were collected in September 2008 and July 2010 for $^{14}$C, $\delta^{13}$C, $\delta^{15}$N and C/N measurements. Three of these are from the Alster, the other seven from the Trave.

Stable isotope measurements The carbon content of aquatic plants was reported to be around 40% (Spencer et al., 1997). 3.5 to 4.5 mg fractions of the freeze-dried, but otherwise un-pre-treated, water plants were thus combusted in order to yield enough CO$_2$ for $^{14}$C dating and $\delta^{13}$C measurement (about 1.2 mgC). The samples have carbon fractions between 22% and 42% (see table). It could thus be suggested to preferentially combust larger samples of $\approx$4.5 mg, but larger samples could yield such a large amount of gasses during combustion that the quartz tube could explode; this happened for three samples with sample sizes of 5.41, 5.62 and 6.23 mg, respectively. Floating leaves tend to have higher carbon fractions than submerged plants or parts of plants. On average, floating leaves have a carbon fraction of $0.410 \pm 0.022$, submerged plants and parts of plants $0.295 \pm 0.057$. No other measured parameter distinguishes between subm. and floating plants.

C/N ratios of aquatic plants from Alster and Trave span a large range from 7.5 to 20.5 (Figure 6.8), thus ranging from typical values of algae to those of terrestrial matter (Meyers and Teranes, 2001). The majority (6 out of 10) of the aquatic plants analysed here, however, has C/N ratios between 10 and 11.5. Also the range of $\delta^{13}$C values is large for the plants analysed here and spans from -34.2 to -17.5‰. This reduces to -31.6 to -25.4‰ when excluding the two extreme values. The $\delta^{13}$C values of bicarbonate in the rivers are approximately -11‰ for both rivers in September 2008, and -14‰ (Alster) and -12‰ (Trave) in July 2010. The normal $\delta^{13}$C shift from bicarbonate to plant cell is 18-19‰ (Olsson and Kaup, 2001). The water plants would thus be expected to have $\delta^{13}$C values between -29 and -33‰. However, when productivity is high or the DIC pool is limited, higher values can occur and even zero fractionation is possible (see section 2.3 and e.g. Higham et al., 2010). The CO$_2$ in the water can be almost 10‰ lighter than the HCO$_3^-$ . However, the dominating DIC species in the rivers analysed here is bicarbonate. Plants utilising CO$_2$ experience thus a limited carbon pool and...
Table 6.5: Stable isotope measurements of aquatic plants from Alster (A) and Trave (T). Subm. plant = submerged plant, Subm./float. = Submerged plant with floating leaves.

<table>
<thead>
<tr>
<th>River, Date</th>
<th>AAR</th>
<th>Species</th>
<th>Carbon fraction</th>
<th>C/N ratio</th>
<th>δ¹³C</th>
<th>δ¹⁵N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Sep 08</td>
<td>12873</td>
<td>subm. plant</td>
<td>0.221±0.132</td>
<td>7.54±0.56</td>
<td>-31.62±0.23</td>
<td>12.63±0.58</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>14334</td>
<td>Nuphar leaf</td>
<td>0.419±0.209</td>
<td>10.02±1.74</td>
<td>-31.5±0.05</td>
<td>10.4±0.27</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>14335</td>
<td>Nuphar petiole</td>
<td>0.364±0.038</td>
<td>17.58±3.20</td>
<td>-31.24±0.05</td>
<td>10.39±0.49</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12870</td>
<td>subm. plant</td>
<td>0.263±0.022</td>
<td>10.36±0.68</td>
<td>-25.42±0.46</td>
<td>9.89±0.52</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12871</td>
<td>floating plant</td>
<td>0.377±0.021</td>
<td>10.94±0.83</td>
<td>-28.09±0.73</td>
<td>12.05±0.55</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12872</td>
<td>subm. plant</td>
<td>0.255±0.001</td>
<td>11.54±0.46</td>
<td>-17.4±1.88</td>
<td>6.81±2.51</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14336</td>
<td>subm. plant</td>
<td>0.319±0.004</td>
<td>11.58±0.86</td>
<td>-34.22±0.05</td>
<td>12.82±0.15</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14337</td>
<td>subm./float.</td>
<td>0.427±0.006</td>
<td>7.51±0.79</td>
<td>-26.95±0.05</td>
<td>-3.35±0.40</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14338</td>
<td>Nuphar leaf</td>
<td>0.415±0.017</td>
<td>10.18±1.40</td>
<td>-27.52±0.05</td>
<td>7.86±0.23</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14339</td>
<td>Nuphar petiole</td>
<td>0.350±0.007</td>
<td>20.51±0.49</td>
<td>-26.67±0.10</td>
<td>5.35±0.12</td>
</tr>
</tbody>
</table>

Table 6.6: δ¹³C determinations of aquatic plants from Alster (A) and Trave (T). Subm. plant = submerged plant, Subm./float. = Submerged plant with floating leaves. Nuphar = Nuphar lutea, yellow water lily, sampled both at the tip of the leaf and at the stem end of the petiole (stem).

<table>
<thead>
<tr>
<th>River, Date</th>
<th>AAR</th>
<th>Species</th>
<th>pmC</th>
<th>¹³C age (yr)</th>
<th>Res. age (¹⁴C yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Sep 08</td>
<td>12873</td>
<td>subm. plant</td>
<td>75.36±0.38</td>
<td>2273±41</td>
<td>2604±41</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>14334</td>
<td>Nuphar leaf</td>
<td>76.83±0.24</td>
<td>2117±25</td>
<td>2472±25</td>
</tr>
<tr>
<td>A, Jul 10</td>
<td>14335</td>
<td>Nuphar petiole</td>
<td>78.51±0.23</td>
<td>1944±24</td>
<td>2299±24</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12870</td>
<td>subm. plant</td>
<td>100.93±0.44</td>
<td>-74±35</td>
<td>347±35</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12871</td>
<td>floating plant</td>
<td>89.64±0.41</td>
<td>879±37</td>
<td>1300±37</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12872</td>
<td>subm. plant</td>
<td>80.93±0.55</td>
<td>1700±55</td>
<td>2120±54</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14336</td>
<td>subm. plant</td>
<td>78.80±0.24</td>
<td>1914±24</td>
<td>2269±23</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14337</td>
<td>subm./float.</td>
<td>85.45±0.24</td>
<td>1263±23</td>
<td>1618±23</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14338</td>
<td>Nuphar leaf</td>
<td>96.48±0.24</td>
<td>288±20</td>
<td>643±20</td>
</tr>
<tr>
<td>T, Jul 10</td>
<td>14339</td>
<td>Nuphar petiole</td>
<td>97.04±0.30</td>
<td>241±25</td>
<td>596±25</td>
</tr>
</tbody>
</table>

Table 6.6: ¹⁴C determinations of aquatic plants from Alster and Trave. Subm. plant = submerged plant, Subm./float. = Submerged plant with floating leaves. Nuphar = Nuphar lutea, yellow water lily, sampled both at the tip of the leaf and at the stem end of the petiole (stem). The reservoir age is estimated by comparing the pmC of the plant with the average pmC of the atmosphere during the preceding growing season (table 6.2 and equation 2.9).

Figure 6.7: ¹⁴C ages and relative sampling depth (surface to bottom, c. 1m deep) of aquatic plants and animals. Photos/drawings not to scale. Feather: mallard (Anas platyrhynchos), larger fish: roach (Rutilus rutilus), smaller fish: spined loach (Cobitis taenia), floating leaves: yellow water lily (Nuphar lutea), bivalve shell: probably Unio sp.
discern whether aquatic forms (Hutchinson, 1975, and references therein), so it is certainly able to assimilate \( \text{CO}_2 \). As explained earlier, \( \delta^{13}\text{C} \) values of aquatic plant cannot be used to distinguish \( \text{HCO}_3^- \) photosynthesis from \( \text{CO}_2 \) photosynthesis (section 2.3).

**14C dating** General remarks and a literature review about radiocarbon dating of aquatic plants can be found in section 2.1.4. The aquatic plants from Alster and Trave have \( ^{14}\text{C} \) ages between -74 and 2273 BP. Comparison with the average \( ^{14}\text{C} \) level of the atmosphere during the preceding growth season (Levin et al., 2010, and pers. comm. I. Levin 2012) yielded estimated reservoir ages between 347 and 2700 years. Just like the \( \delta^{13}\text{C} \) values, \( ^{14}\text{C} \) ages do not differ systematically between submerged and floating leaves. The \( ^{14}\text{C} \) age range of the plants overlaps with that of the water (\( ^{14}\text{C} \) age between 1170 and 2620 BP), but is shifted towards lower values.

Two leaves of *Nuphar lutea*, one from the Alster and one from the Trave, have been subsampled twice, at the bottom of the petiole (stem) and at the tip of the leaf. In both cases, the tip of the leaf is slightly older than the end of the petiole, and both sub-samples show a substantial reservoir effect. The estimated reservoir age of the *Nuphar lutea* from the Trave is 600–640 \( ^{14}\text{C} \) years, from the Alster, 2300–2500 \( ^{14}\text{C} \) years, although the leaf is floating. *Nuphar lutea* assimilates \( \text{CO}_2 \) (Birks, 2001) and can even have terrestrial forms (Hutchinson, 1975, and references therein), so it is certainly able to assimilate \( \text{CO}_2 \) from the air. One would thus expect the leaf to have a \( ^{14}\text{C} \) age closer to atmospheric values, and not the high reservoir age measured. *Nuphar lutea* roots strongly in the bottom of the rivers and stores nutrients from previous growing seasons in the rhizome, which are used for growth in early spring. During the proceeding years, the atmospheric \( ^{14}\text{C} \) level had been higher because of bomb \( ^{14}\text{C} \) (section 2.1.3). Photosynthetic products stored in the rhizome and used for growth of the petioles are thus likely to have higher \( ^{14}\text{C} \) levels than parts of the plants that grew later, using nutrients from photosynthesis during the current growing season. Although the whole plant has a high reservoir effect, the \( ^{14}\text{C} \) age of the petiole is lowered as a result of bomb carbon assimilated during the previous years.

### 6.2.3 Aquatic animals

Radiocarbon dates and stable isotope measurements of aquatic animals are presented in table 6.7 and figure 6.6.

From an uncooked roach fish bone, collagen was extracted for radiocarbon dating. Another bone from the same fish was cooked during the preparation of a food crust. Afterwards, collagen was extracted with the same method as for the uncooked bone (described in chapter 3), including ultrafiltration. The collagen yield of the cooked bone was expected to be smaller than that of the uncooked bone, as collagen begins to degrade at 60°C (Richter, 1986). However, the collagen yields of both samples were high: 102 mg collagen per g sample for the uncooked and even 130 mg collagen per g sample for the cooked bone. Collagen degradation during cooking did not happen. However, the fish was only cooked until it was done and ready for consumption. This was the case at a water temperature of 77°C, and the temperature of the fish bones might have been even lower. In any case, collagen degradation of fish bones cannot be used as an indicator of cooking of the fish, as proposed by (Richter, 1986).

\( \delta^{13}\text{C} \) values of the shells are comparable to those found in shells in rivers and streams (Keith et al., 1964). In North American rivers and streams, the mean values of shell isotope ratios were \( \delta^{13}\text{C} = -11.80\%e \) and \( \delta^{18}\text{O} = -8.45\%e \). \( \delta^{13}\text{C} \) could be as low as -15.16\%e and as high as -8.32\%e. The range of \( \delta^{18}\text{O} \) values was from -4.29\%e to -10.24\%e. \( \delta^{13}\text{C} \) and \( \delta^{18}\text{O} \) of the bivalve shell from the Alster are comparable to pelecypods from Meramec River, Missouri. \( \delta^{18}\text{O} \) of the snail shell is comparable to several samples in Keith et al. (1964), whereas \( \delta^{13}\text{C} \) values as low as the one from the Alster only are found at one site (Keith et al., 1964). In good agreement with the tendency found in \( \delta^{13}\text{C} \) values, the \( ^{14}\text{C} \) ages of the snail and bivalve from the Alster are also lower than the ages of three fluvial shells which were collected alive and had...
### 6.3 Food crusts on pottery

In this section, I will investigate whether the reservoir age of the ingredients is reflected in the food crust and whether stable isotope measurements can be used to identify the ingredients. Experimental food crusts were produced from known ingredients to have reference material available for comparison with archaeological food crusts.

Three series of food crust experiments were conducted, one in August 2007, one in September 2008 and one in June 2012. Samples from the last series of experiments haven’t been analysed yet, but observations from these will be included into the following discussion. In 2007, the objective was to prove the possibility of a freshwater reservoir effect in food crusts on pottery and to show that the age of ingredients and food crust is the same, irrespective of the 

14C age of the cooking water. Therefore, two food crusts were produced; one from freshwater fish and one from wild boar meat. In 2008, mixed ingredients with different isotope values and 14C ages plants were used. Their effect on the isotope values and 14C age of the food crusts was examined. Plants and sea fish were included, but also freshwater fish and meat of a terrestrial animal were used. Mixtures of different ingredients were prepared. In 2012, the range of ingredients was again broadened and included meat, freshwater and marine fish, wild plants, cereals (both C3 and C4), and milk. Additionally, multiple cooking of different ingredients with different isotope values and 14C was done. One objective at the last series of experiments was also the analysis and dating of lipids absorbed in the clay.

#### 6.3.1 Experiments: production of pottery

To copy the prehistorical situation best possible, copies of Stone Age pottery were produced. In 2007 and 2008, pointed base vessels (the typical pottery of the Ertebølle culture) were formed by Harm Paulsen, experimental archaeologist in Schleswig. In 2012, copies of Ertebølle pottery were formed by Dr. Katerina Glykou, archaeologist in Schleswig, while copies of e.g. Narva pottery were formed by Dr. Henny Piezonka, Berlin. The pots were tempered with crushed red granite (see picture 6.9). It is rela-

<table>
<thead>
<tr>
<th>River, Date</th>
<th>AAR</th>
<th>Species</th>
<th>pmC</th>
<th>14C age (14C yrs BP)</th>
<th>Res. age estimate (14C yrs BP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, Sep 07</td>
<td>1140</td>
<td>Mussel shell (probably Unio sp.)</td>
<td>85.68±0.37</td>
<td>1214±34</td>
<td>1654±35</td>
</tr>
<tr>
<td>A, Sep 07</td>
<td>1141</td>
<td>Snail shell</td>
<td>94.75±0.37</td>
<td>433±32</td>
<td>869±34</td>
</tr>
<tr>
<td>A, Sep 07</td>
<td>1142</td>
<td>Roach, bone collagen</td>
<td>97.27±0.35</td>
<td>223±29</td>
<td>660±33</td>
</tr>
<tr>
<td>T, Sep 07</td>
<td>1139</td>
<td>Roach, bone collagen</td>
<td>96.51±0.38</td>
<td>285±32</td>
<td>727±33</td>
</tr>
<tr>
<td>T, Sep 07</td>
<td>1139</td>
<td>Roach, bone collagen (from cooked bone)</td>
<td>97.01±0.34</td>
<td>244±28</td>
<td>685±25</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12874</td>
<td>mallard feather</td>
<td>104.77±0.41</td>
<td>-374±32</td>
<td>47±31</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12875</td>
<td>spined loach</td>
<td>81.29±0.39</td>
<td>1664±39</td>
<td>2085±39</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12876</td>
<td>crayfish</td>
<td>84.37±0.42</td>
<td>1365±40</td>
<td>1787±40</td>
</tr>
<tr>
<td>T, Sep 08</td>
<td>12878</td>
<td>Roach, flesh</td>
<td>99.17±0.40</td>
<td>67±32</td>
<td>488±32</td>
</tr>
</tbody>
</table>

Table 6.7: Radiocarbon dating and stable isotope measurements of animals from Alster and Trave.
6.3. FOOD CRUSTS ON POTTERY

6.3.1 The mixed firing atmosphere with oxidising and reducing conditions

Despite our efforts with drying and slowly heating the pottery, we experienced some losses during the firing. In 2007, two of the pots lost their pointed bases. In 2008, all the pots remained undamaged. In 2012, one large Narva-pot burst. A large pointed-base vessel cracked, but could still be used for cooking (the cracks filled with food which charred and sealed the pot).

6.3.2 Experiments: cooking with Stone Age pottery

The main purpose of the cooking experiments was the production of food crusts on the pottery as a reference material for the analysis of prehistoric food crusts. In addition to that, we were able to assess the usability of the vessels and e.g. the effect of different kinds of fireplaces on the cooking process.

Table 6.8 displays the plant species used in the experiments together with their wild forms possibly used in the Stone Age. The fish and animal species chosen for the experiments had also been used in the Ertebølle culture and are assumed to have changed very little during the last 7000 years. All vegetable plants are C₃ plants. There are only very few edible C₄ plants native to Europe, such as purslane (Portulaca oleracea). We can therefore consider that C₄ plants were insignificant in Stone Age nutrition. However, for the third series of experiments, some C₄ cereals were included for providing, together with the other ingredients, a large range of initial δ¹³C values. In 2008, plants from organic irrespective of how well the individual plants and animals are, they are all potentially affected by modern agriculture or anthropogenic environmental changes.

Table 6.9 shows the “recipes” for the mixtures that were cooked in copies of Ertebølle pointed-base vessels. The following mixtures were chosen because they promised interesting isotope results:

- plant food only
- marine fish and plant
- freshwater fish and plant
- terrestrial herbivore and plant
- terrestrial herbivore and marine fish
- marine fish and C₃ cereal
- terrestrial herbivore and plant in the first cooking procedure, marine fish and plant in the second
- marine fish and plant in the first cooking procedure, terrestrial herbivore and plant in the second

These conditions are comparable to the assumed prehistorical open firing, described by Tite (2003): The bonfire reaches the maximum temperature in 20-30 minutes, while the maximum temperature is maintained only for a few minutes. A temperature of about 710°C was measured in the outer parts of the fire. With our instruments, we were not able to measure the temperature in the central parts, but it can be assumed that the temperature there was at least that high. This is again comparable to the archaeological experiences: in an open firing, maximum temperatures reach from 500 to 900°C, in most cases between 600 and 800°C. The firing atmosphere in an open fire can change rapidly from reducing to oxidising, and fully oxidising conditions are reached very seldom, because the pottery is in intimate contact with smoky and sooty fuel (Tite, 2003). The latter description also fits to our pots: They have an irregular colour, partly reddish and partly dark, reflecting the mixed firing atmosphere with oxidising and reducing conditions (figure 6.10).

First, a spot of soil was cleaned of grass and levelled. This place was dried and warmed by a fire, because firing the pots directly on the cool soil could cause them to break, due to the temperature differences between soil and fire (pers. comm. H. Paulsen 2007). The firing of the pottery is illustrated in figure 6.10. When this first fire was almost completely burnt down, it was pulled apart and the pots were placed in the middle, with the top facing down. Now, the ring of embers surrounding the pots was fed with more firewood and slowly brought closer to the pots, so they heated up slowly. Small portions of glowing embers were also placed between the pots. The slow heating process is necessary because the thick walls crack easily when there are too high temperature differences between within the pot. Especially the thick pointed bases are very fragile, as they might not be completely dry in the middle.

When the fire finally covered the pots, ca. 30 minutes after the pots had been placed onto the firing site, it was steadily enlarged. A large fire was maintained for c. 20 minutes. After that, the fire was left to burn down to ashes, which took about two hours, and the pots were carefully rolled away from the firing site to cool down (figure 6.10).

These conditions are comparable to the assumed prehistorical open firing, described by Tite (2003): The bonfire reaches the maximum temperature in 20-30 minutes, while the maximum temperature is maintained only for a few minutes. A temperature of about 710°C was measured in the outer parts of the fire. With our instruments, we were not able to measure the temperature in the central parts, but it can be assumed that the temperature there was at least that high. This is again comparable to the archaeological experiences: in an open firing, maximum temperatures reach from 500 to 900°C, in most cases between 600 and 800°C. The firing atmosphere in an open fire can change rapidly from reducing to oxidising, and fully oxidising conditions are reached very seldom, because the pottery is in intimate contact with smoky and sooty fuel (Tite, 2003). The latter description also fits to our pots: They have an irregular colour, partly reddish and partly dark, reflecting
Figure 6.9: Rebuilding a pointed-base vessel in the so-called U-technique. Clay and temper (crushed red granite) are mixed and the pointed base is formed. Coils are added to build up the vessel.

- hazelnut and freshwater fish
- marine fish, terrestrial herbivore and plant
- C₄ cereals and bovine milk

The pointed-base vessels are well suited for cooking a variety of ingredients. Different kinds of fireplace can be used; the pots can be placed onto three stones over a small fire, or they can be placed directly into a mixture of glowing embers, ashes, and pieces of firewood. In both cases, the heavy pointed base gives stability and prevents the pot from tipping. Experiments with Ertebølle pottery had been performed quite early (see also section 2.4.1). In the 1930s, it was attempted to boil water in Ertebølle pots. As this did not work, and the water evaporated through the pores before boiling, it was concluded that the Ertebølle pottery was used for making salt from sea water by evaporation at 70-90°C (Klinge, 1932, 1934). However, this explanation was soon discarded, as the same type of pottery was found at inland sites (Mathiassen, 1935). Later experiments showed that the presence of fat or starch in the food would seal the pores and made it possible to boil the ingredients (Andersen and Malmros, 1984). However, our experiments with authentic copies of Ertebølle pottery showed that it is possible to boil pure water in the pots and disprove thus the conclusions from the earlier experiments. It was suggested that it is more probable that the pots were placed in hot em-
Figure 6.10: Firing of the pointed-base vessels. The firing site is prepared, and the pots are placed on the pre-heated ground. The fire is brought closer to the pots and enlarged. The fire is left to burn down. After firing, the pots show signs of oxidising and reducing firing. Photographs by Katerina Glykou

bers and ashes than on an open fire, as this would have been safer for the fragile pots (Andersen and Malmros, 1984). However, our experiments showed that both is possible without breaking the vessels.

The temperature in the pots during the cooking and charring experiments in September 2008 were recorded (Figure 6.11). The temperature profiles were similar in all the pots. It was therefore not considered necessary to monitor the temperatures during the cooking experiments in 2012. In all cases, the temperature increases to 100°C during the first 10-20 minutes. The formation of food crusts begins after 30 to 90 minutes. When the entire water is evaporated, the temperature increases further. Temperatures as high as 300°C can be reached. At different moments, samples were taken from the pots. These moments are marked with numbers in figure 6.11. Table 6.10 summarizes all the samples that were collected from the experiments in 2008. During all three series of experiments, in 2007, 2008 and 2012, it was observed that
Species possibly used in the Stone Age | Species chosen for experiments
---|---
Seakale | Brussels sprouts
*Crambe maritima* | *Brassica oleracea var. gemmifera*
Wild celery | Celery stalks
*Apium graveolens* | *Apium graveolens var. dulce*
Wild carrot | Carrot
*Daucus carota* | *Daucus carota ssp. sativus*
Common scurvy-grass | Rocket
*Cochlearia officinalis* | *Diplotaxis tenuifolia / Eruca sativa*

Species collected for the experiment that most likely were used in the Stone Age
Greater Plantain | *Plantago major*
Dandelion | *Taraxacum officinale*
Stinging nettle | *Urtica dioica*
Hazelnut | *Corylus avellana*

Species used in the experiment that most likely not were used in the Stone Age, but give interesting isotopic results
Spelt | *Triticum aestivum ssp. spelta*
Amaranth | *Amaranthus*
Millet | Different species are sold as millet

Table 6.8: Ingredients for food crusts experiments: which samples were used, and what is the prehistoric plant they are expected to be similar with?

Food crusts do not necessarily form during cooking. Crust formation takes so much time and energy that it is unlikely to have happened very often in the Stone Age. Food crusts that covered the entire lower half of the inner surface of the pot either contained substantial amounts of fat (like the wild boar meat) or of homogeneous starchy ingredients (e.g. milk, ground cereals or hazelnuts). In the case of vegetables, lean meat and fish, single pieces of the foodstuff charred, often without adhering to the pottery. It is possible that the thick homogeneous food crusts found on archaeological potsherds form after repeated cooking, not a single “accident”. In two pots, we cooked two mixtures, terrestrial herbivore and plant in the first cooking procedure, marine fish and plant in the second; vice versa in the other pot. However, even without cleaning the pot in between, no signs of crust formation were observed.

The different materials that can be dated or analysed from prehistoric potsherds are shown in figure 6.12.

### 6.3.3 Stable isotope and ¹⁴C measurements

This section shows the range of stable isotope values and radiocarbon ages for different modern ingredients and how they change during cooking, mixing and charring. Stable isotope measurements on some of the archaeological food crusts (section 6.4) will be included in the discussion.

#### Stable isotope values of ingredients

In the second series of food crust experiments, in September 2008, the isotope values of the raw ingredients were measured. The same is planned for the ingredients from the experiments in 2012. The ingredients themselves are not comparable to Mesolithic food resources, as modern agriculture can have a large influence on the isotope values (e.g. fertilizer for cultivated plants or modern feeding patterns for domesticated animals). However, their isotope values are needed for comparison with the isotope values of the resulting food crusts. The isotope values of the ingredients are displayed in table 6.11 and figure 6.13.

The δ¹³C values of the vegetables span from -30.27 to -26.89‰, their δ¹⁵N values are in the range from 2.05 to 10.45‰. This is a large variation compared to the standard values that are assumed for plants, δ¹³C=-25‰ and δ¹⁵N=3‰, but in the range of isotopic values for other modern cultivated plants. Bonnall et al. (1997) measured δ¹³C values between -26 and -23‰ and δ¹⁵N values from 4.5 to 8.5‰, while van der Merwe (1982) found δ¹³C values between -30.1 and -23.7 for four modern crops. The δ¹³C val-
### Table 6.9: “Recipes” for the food crust experiments in September 2008 and June 2012.

<table>
<thead>
<tr>
<th>Pot</th>
<th>Ingredient</th>
<th>Mass [g]</th>
<th>Percentage of solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008-1</td>
<td>celery stalks</td>
<td>128</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>carrots</td>
<td>90</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>brussels sprouts</td>
<td>120</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>119</td>
<td>—</td>
</tr>
<tr>
<td>2008-2</td>
<td>cod</td>
<td>157</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>celery</td>
<td>159</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>405</td>
<td>—</td>
</tr>
<tr>
<td>2008-3</td>
<td>rocket</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>chard</td>
<td>60</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>fish (roach)</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>575</td>
<td>—</td>
</tr>
<tr>
<td>2008-4</td>
<td>plaice</td>
<td>111</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>roe deer meat</td>
<td>111</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>850</td>
<td>—</td>
</tr>
<tr>
<td>2008-5</td>
<td>herring</td>
<td>90</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>spelt</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>2012-1</td>
<td>roe deer meat</td>
<td>200</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>plantain</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>2012-2a</td>
<td>roe deer meat</td>
<td>200</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>plantain</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>2012-2b</td>
<td>cod</td>
<td>130</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>dandelion</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>2012-3a</td>
<td>cod</td>
<td>130</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>dandelion</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>2012-3b</td>
<td>roe deer meat</td>
<td>200</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>plantain</td>
<td>30</td>
<td>13</td>
</tr>
<tr>
<td>2012-4</td>
<td>ground hazelnut</td>
<td>100</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>carp</td>
<td>440</td>
<td>81</td>
</tr>
<tr>
<td>2012-5</td>
<td>cod</td>
<td>170</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>roe deer meat</td>
<td>260</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>nettle</td>
<td>40</td>
<td>9</td>
</tr>
<tr>
<td>2012-6</td>
<td>amaranth</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>millet</td>
<td>100</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>milk, 1L</td>
<td>125 (solids)</td>
<td>38</td>
</tr>
</tbody>
</table>

\[ \delta^{13}C \] of flesh and bones

Bone collagen of a roach was analysed, and meat from the same fish was used to produce a crust. The difference between the bones and the crust is 1.5 to 3‰ for the fresh and 3 to 4.5‰ for the cooked bone, which is the same order of magnitude as that between flesh and bones of fish. Fish flesh was found to be 1.5 to 4‰ more negative in [\( \delta^{13}C \)] than bone, whereas differences around 5‰ have been reported for terrestrial animals (van der Merwe, 1982; Lanting and van der Plicht, 1998; Katzenberg et al., 2000, 1995, section 2.4.2). Stone Age pike bones from Denmark had [\( \delta^{13}C \)] values as high as -21.2‰. None of the modern fish flesh samples from the same region had [\( \delta^{13}C \)] values over -26‰ (Fischer and Heinemeier,
2003). This indicates that the shift of 5% between flesh and bone collagen, which is typical in herbivores, also can occur in fish, although it is complicated to compare modern with Stone Age values.

The roe deer had isotope values of $\delta^{13}C = -26.24$% and $\delta^{15}N = 8.69$, and is thus in the range of domesticated animals (Bonsall et al., 1997). Its $\delta^{15}N$ value is higher than that of wild herbivores, which had a range of 1-6% and an average of 3.1% (Schwarz, 1991). The roe deer meat was bought at a butcher’s shop, so the animal was probably not wild, but fed with a similar diet as domesticated animals.

The $\delta^{13}C$ value of the roach flesh used in the experiments in 2008 (Table 6.11) is with -22% surprisingly high and almost marine. For comparison, the roach food crust, made one year earlier from a roach from the same river, had $\delta^{13}C = -29%$. The fishbones of roach from the rivers Alster and Trave had $\delta^{13}C$ between -24 and -26%. $\delta^{13}C$ values of flesh of these fish would have been even more negative. The roach
6.3. FOOD CRUSTS ON POTTERY

Figure 6.12: Different materials from archaeological pottery for radiocarbon dating (left) and biomolecular analyses (lipids and stable isotopes, right).

flesh from 2008 is thus an outlier, also when compared with literature values for freshwater fish. Lanning and van der Plicht (1998), for example, analysed flesh of freshwater fish from the Netherlands. It resulted in δ13C values between -37.2 and -27.5‰. In a totally different environment, however, heavily enriched freshwater fish has been found. Shishlina et al. (2007) report δ13C = -16.5‰ for prehistoric bones of pike from the north-western Caspian steppe.

Fat has generally lower δ13C values than meat. Beef fat and lamb fat, for example, have δ13C = -30‰ and -33‰, respectively (Bonsall et al., 1997; Browman, 1981). Fatty fish is accordingly expected to have lower δ13C values than lean fish. Therefore, both herring and cod were used in the experiments in 2012.

Figure 6.13: δ13C and δ15N values of the ingredients for the food crust experiments in September 2008. See table 6.11 for the values.
<table>
<thead>
<tr>
<th>Pot</th>
<th>Sample ID</th>
<th>Material</th>
<th>Extracted...</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13575</td>
<td>raw celery</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13573</td>
<td>raw Brussels sprout</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13572</td>
<td>raw carrot</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13814</td>
<td>cooked vegetables</td>
<td>figure 6.11b: 4</td>
</tr>
<tr>
<td></td>
<td>13868</td>
<td>cooked vegetables</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13869</td>
<td>cooked vegetables</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>13575</td>
<td>raw celery</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13579</td>
<td>raw cod</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13815</td>
<td>cooked fish and vegetables</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13877</td>
<td>cooked vegetables</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13878</td>
<td>cooked fish</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13880</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13881</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13882</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13883</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13884</td>
<td>crust from boiling over</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13885</td>
<td>outer crust, probably soot</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>13574</td>
<td>raw rocket</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13571</td>
<td>raw chard</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13578</td>
<td>raw roach</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13816</td>
<td>cooked fish and vegetables</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13886</td>
<td>cooked fish and vegetables</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13887</td>
<td>fish and fishbones, slightly charred</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13888</td>
<td>uncharred crust from upper rim</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13889</td>
<td>crust, just below rim</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>13574</td>
<td>raw rocket</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13571</td>
<td>raw chard</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13576</td>
<td>raw roe deer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13817</td>
<td>cooked meat and vegetables</td>
<td></td>
</tr>
<tr>
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<td>13818</td>
<td>cooked meat and vegetables</td>
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<tr>
<td></td>
<td>13890</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13891</td>
<td>crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13892</td>
<td>soot (outside)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>13577</td>
<td>raw plaice</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13576</td>
<td>raw roe deer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13819</td>
<td>cooked meat</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13820</td>
<td>cooked fish</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13821</td>
<td>froth from upper rim</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13822</td>
<td>fish and meat with charred crust</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13893</td>
<td>crust 1 upper rim</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13894</td>
<td>crust 2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13895</td>
<td>crust 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13896</td>
<td>crust 4</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.10: Samples from the food crust experiments in September 2008
### Table 6.11: Stable isotope measurements of the ingredients for the food crust experiments in September 2008.

Measurements on cooked ingredients, cooked mixtures and food crusts are presented in Table 6.13.
Change of isotopic ratios during cooking and charring

The cooked ingredients have only been measured for the 5 mixture-stews. The expected isotope ratios of the mixtures were calculated from the isotope ratios, carbon and nitrogen fractions of the ingredients and from their percentages in the mixture (see recipes in table 6.9). The uncertainties of the expected values are not drawn in the diagrams for the sake of clarity. They are relatively large because they combine the uncertainties of the measured isotope ratio, C or N fraction, and the weighed amount of ingredients.

Figures 6.14 to 6.18 show how stable isotope values change with cooking. In all cases, the isotopic values of the mixture are close to one of the ingredients, or close to a mixing line, or both. There are only two exceptions. First, the vegetable mixture, where the isotopic values of the cooked mixture are more than one standard deviation away from the carrot-celery mixing line (see figure 6.14). Still, this can be just a statistical outlier. Second, the δ15N value of the vegetables that were cooked together with roe deer meat is negative, and much lower than the raw vegetables’ δ15N values. This sample had a low nitrogen content (nitrogen fraction=0.063), but the δ15N value could be measured by taking a large sample and diluting the CO₂. Three subsamples were measured independently (in different sample lists/MS runs on different days), producing values of δ15N=-2.14±0.35‰, -0.68±0.70‰ and -1.97±0.38‰, so that the measurement is reliable, although the variation is quite large.

For vegetables and cod, the δ15N values increase through cooking. This increase is especially large for vegetables that have been cooked together with fish. For vegetables and roe deer, the δ15N values of the vegetable decrease, while the δ13C values increase (become less negative).

The largest change in δ13C values is observed for Brussels sprouts which are cooked with carrot and celery. It is +1.16‰. The δ13C value of the carrot from the same stew changes by -0.70‰. The largest δ15N change occurs for celery which cooked together with cod and increases with 5.39‰. The δ15N value of roach with is cooked together with vegetables decreases by 1.24‰. On average, δ13C values change with +0.22±0.60‰, δ15N values with +0.69±2.05‰. The average changes for meat and fish are 0.14±0.39 in δ13C values and 0.56±2.41 in δ15N. For vegetables, the changes are ∆δ13C=0.36±0.96 and ∆δ15N=2.51±2.49.

The cooking of mixtures thus confirms the results of the authors cited in chapter 2, that cooking only slightly changes the isotopic values of different foodstuffs. It should also be noted that the difference between the cooked vegetable mixture and its expected value only is about 1‰, which is in the range of changes that other authors found when cooking ingredients, which was 1 to 1.5‰ (Katzenberg et al., 2000; Abonyi, 1993; Marino and DeNiro, 1987; Bonsall et al., 1997). As neither me nor the cited authors find a certain trend of isotopic change when cooking food, I suggest to add an extra uncertainty of about 1‰ when comparing fresh and cooked ingredients, e.g. when trying to reconstruct ingredients from isotopic values of cooked food.

Celery and cod were cooked together. I compare the carbon and nitrogen fractions of the raw celery and cod (Table 6.11) with those of the cooked celery (Table 6.13) to estimate the amount of fish organic matter that was absorbed by the celery through cooking. The carbon and nitrogen fraction of the raw cod are higher than of the raw celery. The carbon fraction of the celery increases slightly during cooking (from 0.334 to 0.346) while its nitrogen fraction increases substantially (from 0.011 to 0.033). The carbon fraction indicates that the cooked celery contains c. 9% cod organic matter, while the nitrogen fraction indicates 16%. Correspondingly, the δ13C value of the celery increases slightly while the δ15N value increases substantially (Table 6.12). However, as mentioned above, δ15N values increase for both celery and cod, maybe as a result of leaching of substances containing lighter δ15N values.

For the vegetable crust, the cooked mixture and the crust values are in the range that was expected. From the finished crust, two pieces of vegetable that still were recognizable were extracted, one piece of Brussels sprouts and one piece of carrot. Both of them were charred on one side and had their original colour on the other side. The change of isotope ratios for the cooked and the charred vegetable from the raw is in the same direction. In all cases, δ13C values increase. δ13C values decrease by about 0.7‰ for the carrot and increase by 1.1‰ from raw to cooked and 1.8‰

<table>
<thead>
<tr>
<th>Material</th>
<th>δ13C</th>
<th>δ15N</th>
</tr>
</thead>
<tbody>
<tr>
<td>celery</td>
<td>-28.82</td>
<td>10.45</td>
</tr>
<tr>
<td>cooked</td>
<td>-18.73</td>
<td>15.15</td>
</tr>
<tr>
<td>cod</td>
<td>-18.99</td>
<td>15.29</td>
</tr>
</tbody>
</table>

Table 6.12: Isotope ratios of raw and cooked celery and cod.
Figure 6.14: Isotope ratios of ingredients and experimental food crusts. The expected value of the crust is calculated with the relative proportion of the ingredients, their carbon and nitrogen contents and isotope ratios. 

from raw to charred Brussels sprouts.

When cooking roe deer and plaice, $\delta^{15}N$ values decrease.

**Stable isotope measurements of experimental food crusts**  Very high C/N values occur for $\delta^{13}C = -26$ to $-28\%e$ which indicates terrestrial plants. Very high C/N values only occur for rather low $\delta^{15}N$ values which is caused by the fact that plants have low $\delta^{15}N$ and high C/N, in contrast to fish and terrestrial animals.

In total, the experimental food crusts have $\delta^{13}C$ values between c. -31 and -19\%e (not including the “marine wild boar”) and $\delta^{15}N$ values between c. 4 and 19\%. The $\delta^{13}C$ range of the experimental food crusts can be as high as 7\%e for the food crusts from one pot, the $\delta^{15}N$ range about 6\%. In contrast to that, the isotope ratios of the food crusts from the two archaeological inland sites span much smaller intervals. We can conclude that no marine products were used at the inland sites and that only terrestrial plants and animals as well as freshwater fish were consumed there.

The broad ranges of isotope ratios of modern food crusts are reflected in the ranges of food crust measurements from Neustadt. Marine fish and terrestrial plants and animals were certainly consumed there, but the consumption of freshwater fish can not be excluded.

**A marine wild boar**  The food crust made on wild boar meat (black squares in figure 6.19) has $\delta^{13}C$ values around -18\%e, which are typical of marine fish and mammals, but relatively low $\delta^{15}N$ values around 8\%. If the wild boar had been fed with marine fish, it would have had higher $\delta^{15}N$ values. A possible explanation is the consumption of C$_4$ plants (see section 2.2.1). As there are virtually no wild C$_4$ plants in Northern Germany, the wild boar had probably not been “wild”, but was raised in a game enclosure, or it lived wild in the forest, but had been fed regularly with maize, a C$_4$ plant. This is a common practice by hunters who want the animals to get used to a certain spot in the forest for easier hunting.

In figure 6.19, I include data by Craig et al. (2011) on experimental food crusts and on archaeological food crusts from Neustadt. Experimental food crusts
Chapter 6. Freshwater Effect in Northern Germany

Cooking of freshwater fish and vegetables (42% roach, 28% chard, 30% rocket)

\[
\begin{align*}
\text{Cl}\text{13C (‰ VPDB)} & \quad \text{Cl}\text{15N (‰ AIR)} \\
-33.00 & -31.00 & -29.00 & -27.00 & -25.00 & -23.00 & -21.00 & -19.00 & -17.00 & -15.00 \\
\text{expected value} & \quad \text{cooked mixture} & \quad \text{roach} & \quad \text{chard} & \quad \text{rocket}
\end{align*}
\]

Figure 6.16: Isotope ratios of ingredients and experimental food crusts. The expected value of the crust is calculated with the relative proportion of the ingredients, their carbon and nitrogen contents and isotope ratios.

Cooking of roe deer and vegetables (50% roe deer meat, 25% rocket, 25% chard)

\[
\begin{align*}
\text{Cl}\text{13C (‰ VPDB)} & \quad \text{Cl}\text{15N (‰ AIR)} \\
-32.00 & -31.00 & -30.00 & -29.00 & -28.00 & -27.00 & -26.00 & -25.00 & -24.00 & -23.00 & -22.00 \\
\text{expected value} & \quad \text{cooked mixture} & \quad \text{rode deer} & \quad \text{rocket} & \quad \text{chard} & \quad \text{cooked meat} & \quad \text{cooked vegetables}
\end{align*}
\]

Figure 6.17: Isotope ratios of ingredients and experimental food crusts. The expected value of the crust is calculated with the relative proportion of the ingredients, their carbon and nitrogen contents and isotope ratios.

with $\delta^{13}$C $>-24.5\%$ include at least some marine fish. This is in contrast to Andersen and Malmros (1984) who interpreted $\delta^{13}$C values of $-22.1\%$ in a food crust as terrestrial, although remains of cod had been found in the crust. Fischer and Heinemeier (2003) interpreted food crust $\delta^{13}$C values $>-26\%$ as indicating a contribution of marine food. However, some of the experimental food crusts have $\delta^{13}$C $>-26\%$ although they are free of marine food. These are roe deer meat with vegetables, freshwater fish with vegetables and Einkorn (see figures 6.19 and 6.21). Furthermore, Fischer and Heinemeier (2003) interpreted food crust $\delta^{13}$C values $<-28\%$ as indicating a contribution of freshwater food. In total, five out of the 21 samples shown in figure 6.21 would have been identified incorrectly when applying the criteria from Fischer and Heinemeier (2003) (e.g. finding a “marine” value in a food crust that does not contain any marine ingredients). Andersen and Malmros (1984) use $\delta^{13}$C values $<-20\%$ as criterion for terrestrial ingredients in a food crust. In fact, all of the experimental food crusts that would be labelled “terrestrial” after their distinction, do contain at least some terrestrial ingredient. All of the food crusts that would be labelled “non-terrestrial” do contain at least some non-terrestrial ingredient. However, there are many food crusts with a marine contribution that have $\delta^{13}$C values $<-20\%$ and a substantial reservoir age (see below), which would not have been distinguished by the $20\%$-criterion.

Craig et al. (2007) analysed stable isotopes as well as lipid biomarkers. They could identify some isotopic ranges that are characterised by specific biomarkers. Their classification is drawn as boxes upon an overview of my measurements on experimental and archaeological food crusts. With the isotopic ranges of Craig et al. (2007), most of my experimental samples would have been classified correctly. However, many of my experimental and archaeological food crusts have higher $\delta^{15}$N values than the samples of Craig et al. (2007).

Radiocarbon dating of experimental food crusts

All aquatic ingredients as well as food crusts containing aquatic resources were radiocarbon dated. The results are presented in table 6.13. Additionally, scatter plots of $\delta^{13}$C and radiocarbon age as well as $\delta^{15}$N and radiocarbon age are shown in figures 6.23 and
6.3. FOOD CRUSTS ON POTTERY

Cooking of roe deer (50%) and plaice (50%)

<table>
<thead>
<tr>
<th>13C (‰ VPDB)</th>
<th>15N (‰ AIR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-33.00</td>
<td>-26.50</td>
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<tr>
<td>-31.00</td>
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<td>-29.00</td>
<td>-24.50</td>
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<td>-27.00</td>
<td>-23.50</td>
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<tr>
<td>-25.00</td>
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<tr>
<td>-19.00</td>
<td>-19.50</td>
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<tr>
<td>-17.00</td>
<td>-18.50</td>
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</table>

expected value

Cooking of roe deer (50%) and plaice (50%)

<table>
<thead>
<tr>
<th>13C (‰ VPDB)</th>
<th>15N (‰ AIR)</th>
</tr>
</thead>
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<tr>
<td>7.50</td>
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<td>10.50</td>
<td>11.50</td>
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<td>8.50</td>
</tr>
<tr>
<td>14.50</td>
<td>7.50</td>
</tr>
</tbody>
</table>

expected value

Figure 6.18: Isotope ratios of ingredients and experimental food crusts. The expected value of the crust is calculated with the relative proportion of the ingredients, their carbon and nitrogen contents and isotope ratios.

6.24. The measured radiocarbon ages are between -1250 and +67 years. Terrestrial plants harvested around September 2008 are expected to have radiocarbon ages around -420 14C years. The radiocarbon age of -427 ± 23 years of the vegetables that had been cooked together with cod (AAR-14021) meets these expectations. Meat of terrestrial animals is expected to be correspondingly slightly “younger” as a result of turnover time in the muscles. AAR-12878, 14013, 14029, 14031 and 14033 are samples of freshwater fish and of the mixture of freshwater fish with vegetables. They reflect a combination of a freshwater reservoir effect (positive radiocarbon ages) with partial admixture of vegetables (-235 14C years). The other samples are expected to show a marine reservoir effect. However, they are all significantly “younger” than the atmosphere, i.e. have even more negative radiocarbon ages.

Isotope ratios of soot Soot consists of carbon in the form of graphite. Soot from e.g. hearth fires furthermore contains substantial amounts of organic compounds. Outer crusts on pottery are a mixture of soot from the fire and food that had boiled over. The isotope ratios of five outer crusts have been measured (Table 6.14). Two of these were experimental food crusts, the other three archaeological. The large range of isotope ratios and C/N values indicates that soot from the combustion of firewood cannot be the only source of the outer crusts. Food that boiled over is one possible explanation. However, the C/N ratios of the experimental food crusts are higher than those of the inner crusts from the same pots (cf. Figure 6.20) which indicates a soot contribution.

A reverse old wood effect Different materials from the cooking and charring of cod with vegetables were 14C-dated. The reservoir ages were estimated for these samples by comparison with atmospheric CO2 (see section 2.1.4). The cooked vegetables have a reservoir age of ≤0 14C years, as expected. The cod is a marine fish, and thus a reservoir age in the order of magnitude of 400 years was expected. However, the cod samples all have negative reservoir ages. This could be a result of bomb carbon in the food chain of the cod (section 2.1.3). The outer crust is even younger. This could be a reverse old wood effect. The wood for our hearth fires was partly collected in the forest surrounding the cooking site, but part of it was used timber. It is thus possible that some of the firewood grew some decades ago, when atmospheric 14C levels were substantially higher due to the bomb effect (section 2.1.3). As the old wood lead to younger (more negative) 14C ages, the bomb spike had reversed the old wood effect. The calendar age ranges of the outer crust are AD 1958-1959 (24.6%) and AD 1987-1990 (70.8% Bronk Ramsey, 2009) which agrees with the interpretation of old timber.
| Table 6.13: $^{14}$C dating and stable isotopes of experimental food crusts. Only $^{14}$C dated samples are listed here. The majority of the purely terrestrial samples has not been $^{14}$C dated. |  

<table>
<thead>
<tr>
<th>AAR</th>
<th>Name</th>
<th>$\delta^{13}$C</th>
<th>$\delta^{15}$N</th>
<th>C/N ratio</th>
<th>C frac.</th>
<th>N frac.</th>
<th>$^{14}$C age</th>
</tr>
</thead>
<tbody>
<tr>
<td>12877</td>
<td>plaice, uncooked</td>
<td>-18.53±0.25</td>
<td>14.03±0.52</td>
<td>3.97±0.28</td>
<td>0.474±0.020</td>
<td>0.138±0.010</td>
<td>-588±32</td>
</tr>
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<td>12878</td>
<td>roach (freshwater fish)</td>
<td>-22.30±0.10</td>
<td>14.86±0.32</td>
<td>3.92±0.28</td>
<td>0.486±0.022</td>
<td>0.144±0.008</td>
<td>67±32</td>
</tr>
<tr>
<td>12879</td>
<td>cod, uncooked</td>
<td>-18.73±0.36</td>
<td>15.15±0.53</td>
<td>3.65±0.24</td>
<td>0.468±0.020</td>
<td>0.150±0.007</td>
<td>-667±34</td>
</tr>
<tr>
<td>14012</td>
<td>cod and vegetables, cooked</td>
<td>-19.61±0.23</td>
<td>14.97±0.19</td>
<td>3.98±0.25</td>
<td>0.481±0.019</td>
<td>0.141±0.007</td>
<td>-604±27</td>
</tr>
<tr>
<td>14013</td>
<td>roach and vegetables, cooked</td>
<td>-23.12±0.15</td>
<td>14.02±0.24</td>
<td>4.29±0.31</td>
<td>0.504±0.021</td>
<td>0.137±0.008</td>
<td>6±27</td>
</tr>
<tr>
<td>14016</td>
<td>plaice and roe</td>
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<td>8.24±0.25</td>
<td>4.00±0.24</td>
<td>0.515±0.024</td>
<td>0.150±0.008</td>
<td>-503±23</td>
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<td>12880</td>
<td>plaice and roe</td>
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<td>13.96±0.36</td>
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<td>0.494±0.020</td>
<td>0.146±0.008</td>
<td>-635±23</td>
</tr>
<tr>
<td>14017</td>
<td>plaice and roe</td>
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<td>13.40±0.59</td>
<td>4.12±0.26</td>
<td>0.500±0.019</td>
<td>0.142±0.007</td>
<td>-623±23</td>
</tr>
<tr>
<td>14018</td>
<td>plaice and roe</td>
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<td>8.04±0.19</td>
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<td>0.524±0.022</td>
<td>0.149±0.008</td>
<td>-403±23</td>
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<td>14021</td>
<td>cod and vegetables, cooked</td>
<td>-28.20±0.15</td>
<td>15.84±0.29</td>
<td>13.78±1.23</td>
<td>0.346±0.007</td>
<td>0.033±0.002</td>
<td>-427±23</td>
</tr>
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<td>14022</td>
<td>cod and vegetables, cooked</td>
<td>-18.99±0.10</td>
<td>15.29±0.46</td>
<td>3.78±0.26</td>
<td>0.501±0.022</td>
<td>0.155±0.008</td>
<td>-660±24</td>
</tr>
<tr>
<td>14023</td>
<td>cod and vegetables, crust</td>
<td>-21.63±0.49</td>
<td>16.21±0.39</td>
<td>10.17±1.37</td>
<td>0.445±0.004</td>
<td>0.048±0.006</td>
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<td>14024</td>
<td>cod and vegetables, crust</td>
<td>-19.08±0.19</td>
<td>16.53±0.15</td>
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<td>0.115±0.007</td>
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<td>14025</td>
<td>cod and vegetables, crust</td>
<td>-20.34±0.46</td>
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<td>0.520±0.039</td>
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<td>-538±22</td>
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<td>14026</td>
<td>cod and vegetables, crust</td>
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<td>17.44±0.31</td>
<td>5.18±0.12</td>
<td>0.613±0.017</td>
<td>0.139±0.007</td>
<td>-557±38</td>
</tr>
<tr>
<td>14027</td>
<td>cod and vegetables, crust</td>
<td>-25.14±0.44</td>
<td>12.87±0.23</td>
<td>6.58±0.39</td>
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<td>14028</td>
<td>cod and vegetables, outer</td>
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<td>12.36±1.71</td>
<td>13.77±4.57</td>
<td>0.636±0.046</td>
<td>0.035±0.009</td>
<td>-1247±27</td>
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<td>14029</td>
<td>roach and vegetables, cooked</td>
<td>-21.55±0.38</td>
<td>13.62±1.16</td>
<td>3.76±0.16</td>
<td>0.477±0.076</td>
<td>0.147±0.025</td>
<td>4±25</td>
</tr>
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<td>14031</td>
<td>roach and vegetables, crust</td>
<td>-26.18±0.80</td>
<td>12.73±0.31</td>
<td>7.99±1.95</td>
<td>0.458±0.073</td>
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<td>14032</td>
<td>roach and vegetables, crust</td>
<td>-24.81±0.15</td>
<td>13.08±0.63</td>
<td>7.03±0.29</td>
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<td>-236±34</td>
</tr>
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<td>14035</td>
<td>plaice and roe</td>
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<td>13.43±0.76</td>
<td>3.89±0.17</td>
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<td>0.150±0.004</td>
<td>-1162±26</td>
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<td>14036</td>
<td>plaice and roe</td>
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<td>13.94±0.73</td>
<td>4.66±0.71</td>
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<td>13.94±0.32</td>
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<td>11.89±0.65</td>
<td>5.82±0.23</td>
<td>0.613±0.012</td>
<td>0.009±0.060</td>
<td>-538±23</td>
</tr>
</tbody>
</table>
6.3. FOOD CRUSTS ON POTTERY

Figure 6.19: Isotope ratios of experimental and archaeological food crusts. Experimental food crusts are shown in different colours, archaeological food crusts are labelled with a letter indicating the site.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta^{13}$C [% PDB]</th>
<th>$\delta^{15}$N [% AIR]</th>
<th>C/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>exp. (cod and vegetables)</td>
<td>-23.38</td>
<td>12.36</td>
<td>13.77</td>
</tr>
<tr>
<td>exp. (roe deer and vegetables)</td>
<td>-25.16</td>
<td>9.56</td>
<td>26.81</td>
</tr>
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<td>archaeological (SLA5-1713)</td>
<td>-28.01</td>
<td>3.39</td>
<td>16.29</td>
</tr>
<tr>
<td>archaeological (Neustadt)</td>
<td>-24.53</td>
<td>12.46</td>
<td>12.75</td>
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<td>archaeological (Neustadt) (base-soluble)</td>
<td>-24.44</td>
<td>12.44</td>
<td></td>
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<tr>
<td>archaeological (Neustadt)</td>
<td>-27.24</td>
<td>10.54</td>
<td>10.56</td>
</tr>
<tr>
<td>archaeological (Neustadt) (base-soluble)</td>
<td>-25.74</td>
<td></td>
<td></td>
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</tbody>
</table>

Table 6.14: Isotope ratios of experimental and archaeological “outer crusts” from pottery.
Figure 6.20: δ¹³C values and C/N ratios of archaeological and experimental food crusts. There are three pairs of values from Kayhude, each containing one pre-treated (AAA) and one not pre-treated subsample from the same sherd. As the values are so close to each other, and the changes in δ¹³C values or C/N ratios are not systematic, I do not indicate on this figure which sample was pre-treated and which not. For an explanation of the “marine” wild boar, see page 123.
6.3. FOOD CRUSTS ON POTTERY

Figure 6.21: $\delta^{13}C$ and $\delta^{15}N$ values of some experimental and archaeological food crusts. With an interpretation from Fischer and Heinemeier (2003).

Figure 6.22: $\delta^{13}C$ and $\delta^{15}N$ values of some experimental and archaeological food crusts. With an interpretation from Craig et al. (2007).

Figure 6.23: Radiocarbon ages and $\delta^{13}C$ values of modern ingredients, mixtures of food stuffs and food crusts.

Figure 6.24: Radiocarbon ages and $\delta^{15}N$ values of modern ingredients, mixtures of food stuffs and food crusts.

Figure 6.25: $\delta^{13}C$ values and $^{14}C$ ages of experimental food crusts. The values obtained for the food crusts made of cod and vegetables are marked.
Effect of pre-treatment

Figure 6.26: Change of δ^{13}C and δ^{15}N ratios of three archaeological food crust samples during chemical pre-treatment.

Figure 6.27: Change of δ^{13}C values and C/N ratios of archaeological food crusts during chemical pre-treatment.

Some of the archaeological food crust samples were very small. Under pre-treatment, some sample material is always lost. It was therefore examined whether reliable stable isotope measurements on archaeological food crusts can be made without previous pre-treatment. Some food crust samples were therefore analysed twice, before and after chemical pre-treatment (AAA, see chapter 3). The results are presented in figures 6.26 and 6.27.

It can be seen that the shifts in isotope ratios are small and not systematic. In the C/N ratio, however, larger shifts are possible and in six cases out of seven, the C/N ratio decreases after the pre-treatment. In conclusion, the chemical pre-treatment of archaeological food crusts can be omitted if the samples otherwise would be too small for isotope measurements. The uncertainty of the δ^{13}C and δ^{15}N values may increase. C/N ratios of unpretreated food crusts should be disregarded and never be compared to C/N ratios of pre-treated food crusts.

I have extracted proteins from three experimental food crusts with the modified Longin-method for the extraction of collagen from bones. 535 mg of wild boar crust, 282 mg of roach crust and 573 mg of porpoise crust were weighed out for protein extraction. I could extract 1-6 mg protein per 1 g of food crust, but not all could be taken out of the pre-treatment vials. The pretreatment yields are: 0.49% for the wild boar food crust, 0.60% for the roach food crust and 0.12% for the porpoise food crust. This is comparable to the yield reported in another study. Segerberg et al. (1991) could extract 3mg amino acids from 1g of food crust, so their pretreatment yield was 0.3%. The pre-treatment yields I measured correspond to the observed fat contents, the more fat, the less protein. In the case of the porpoise, 0 mg of the extracted protein could be taken out of the glass. Also the roach protein samples were too small for reliable measurements. With a carbon fraction of about 0.5 in the protein, and the experience that about 1.5 mg of the sample can stick to the pre-treatment vial and be impossible to extract, I would suggest to use 1 g of food crust to be sure to have a carbon yield of 1 mgC. A yield of 1 mgC in protein extracted from 1 g of food crust has previously been reported (Segerberg et al., 1991). The results from the different pre-treatment procedures are summarized in table 6.15 and figures 6.28, 6.29, 6.30 and 6.31. Note the different scales on the figures. The wild boar has more positive δ^{13}C values than the porpoise because it was probably fed with maize, a C_{4} plant (see section 2.2.1).

The average δ^{13}C value of the roach food crust, which was prepared in 2007, is 2.30±1.23 permil more negative than the bone δ^{13}C value. This is in agreement with the reported differences between flesh and bones (see section 2.4.2). The δ^{15}N value of the food crust is 3.33±0.77 permil higher than the bone value. Unfortunately, I have not been able to find a reference that compared δ^{15}N values of fish bones and flesh. The roach cooked in 2008 has δ^{15}N values similar to the roach fish bones from 2007. Unfortunately, the fish bones from the experiments in 2008 have not been secured and analysed.

Porpoise blubber was cooked in a copy of a pointed-based EBK vessel to produce oil for a lamp. The crust that was formed in the pointed-based vessel during this process has a radiocarbon age which is 655 years
6.3. FOOD CRUSTS ON POTTERY

Wild boar food crust, different pretreatment methods

Roach from the Trave: comparison food crust - bone

Figure 6.28: Stable isotope values of a wild boar food crust that was pre-treated with different methods.

Figure 6.29: Stable isotope values of a roach food crust that was pre-treated with different methods.

“younger” than the uncooked fat. Its $\delta^{13}C$ value is $3.17\%$ higher than that of the fat. During cooking in the pot, the oil from the fat cells liquefied and could be poured off. The crust was probably formed of the residue, i.e. empty fat cells. This explains the difference in $\delta^{13}C$ values. Similar differences had been reported for fat and lean meat of other animals (see section 2.4.2). The fat cells had probably formed when the animal was young and the 14C level in the oceans was higher than today (see section 2.1.3). These cells were then filled with fat from recent metabolism when 14C levels had decreased, hence the age difference.

The small amount of protein that could be extracted from the wild boar food crust made the stable isotope measurement difficult. The $N_2$ and CO$_2$ peak heights were too low for reliable measurements. The collagen $\delta^{13}C$ is different from the normal $\delta^{13}C$, and this is probably due to the too low peak height of the CO$_2$ peak, which only was 1/10 of the required. For roach, there is no difference in isotope values, so the normal pretreatment gives the same results as the more complex collagen extraction. This method should be tested for archaeological food crusts as well, as one might assume that the proteins are more likely to represent the original sample than the bulk organic matter from the food crust that otherwise is used. Furthermore, a better method for taking the samples out of the pretreatment vials has to be found. The samples could for example be transferred to the quartz tubes for combustion (see chapter 3) while still in solution. Alternatively, quartz chippings could be placed in the glasses in which the gelatin solution is dried. When the gelatin solutions dries, a substantial proportion of it would adhere to the quartz chippings instead of the vial. Gelatin and quartz chippings could the be transferred together to a quartz tube for combustion.
6.4 Radiocarbon dating of archaeological samples

For radiocarbon dating, 4-6 mg of extracted lipid are used, whereas 30-40 mg of food crust or 10 mg of soot (weighed prior to pre-treatment) are required. For pre-treatment of charcoal and wood, 15-30 mg were taken. When available, 200-300 mg of drilled or crushed bone powder were pre-treated, but in many cases, the samples were smaller. Pre-treatment procedures are described in chapter 3.

Figures 6.32 and 6.33 show radiocarbon ages of the samples from Kayhude and Schlamersdorf which I processed myself. The lowermost two boxes in each figure include dates for the aquatic and terrestrial context. The other boxes above contain each the radiocarbon dates belonging to the same potsherd.

Likewise, I show the radiocarbon dates from the coastal site Neustadt. There, I only made the seven lipid dates myself, the rest is from the literature (Craig et al., 2011). Neustadt comprised two cultures, the Mesolithic Ertebølle culture (EBK) and the Neolithic Funnel Beaker culture (TRB). 2-σ intervals are given for the dates. The upper boundary of the youngest terrestrial date from the Ertebølle culture, and the lower boundary of the oldest terrestrial date from the Funnel Beaker culture are indicated by vertical lines. The overlap between the two phases, defined in this way, is only about 100 years.

Kayhude In Kayhude, the samples were collected from a relatively undisturbed stone paving (pers. comm. I. Clausen, 2007). The age difference of over 3000 years between the fish and the charcoal from Kayhude is much larger than the reservoir ages that we find for modern fish, but of the same order of magnitude as the reservoir age for modern water and plants. One terrestrial sample has a radiocarbon age of more than 9000 BP. This bone must be an admixture from earlier layers, as it is not only older than the other terrestrial sample from Kayhude, but also older than the oldest finds of the entire Ertebølle culture. This exemplifies that the stone paving where we found our samples cannot be regarded as totally undisturbed. Direct radiocarbon dating of the pottery is thus necessary, as we cannot be sure which terrestrial samples are clearly associated with the pottery.

None of the food crusts are as old as the fish bones, though. The humic fraction of three food crusts has also been dated. The humic fraction is likely to consist of humic acids from the soil, and is thus removed from the samples. Here it is older than the food crusts (Figure 6.32), indicating contamination with an older soil substance.

Schlamersdorf The terrestrial age range of Schlamersdorf complies with earlier charcoal datings from this site (Hartz, 1993b). The age range of terrestrial samples is very broad (Figure 6.33). This does not mean that this site has been inhabited for 1000 14C years. It was probably occupied repeatedly for shorter periods, as archaeological analysis indicated that the site was a hunting or fishing station. The broad terrestrial age range reveals the necessity of direct pottery dating.

Two sub-samples of the food crust AAR-11484 have been dated. One of them was very small, 0.15 mgC, while the other one had half of the optimum size (0.47 mgC). “Normal” samples have about 1 mgC. Within uncertainties, the radiocarbon dates agree. However, the smaller sample is slightly younger. This might be the effect of a constant amount of modern contamination that enters the samples during preparation or measurement. The wildcat bone AAR-11398 and the food crusts AAR-11482 and AAR-11484 had been found quite close to each other. It is therefore probable that they are contemporaneous. Their radiocarbon ages are in fact very similar. If the measurement of the larger sample indicates the correct
6.4. RADIOCARBON DATING OF ARCHAEOLOGICAL SAMPLES

Figure 6.32: Uncalibrated radiocarbon ages of archeological samples from Kayhude/Alster. The plot was made with OxCal 4.1 (Bronk Ramsey, 2009), using a straight line y=x as a “calibration curve”. 2σ-intervals are indicated below the probability distributions of the radiocarbon ages.

...
environment, from the handling during the excavation or later during storage in the archives, this contamination would be expected to have affected both sides of the sherd equally.

In one of the sherds, AAR-11483, we were lucky to find some plant remains that presumably had been incorporated in the clay during the forming of the pottery. Unfortunately, the food crust sample of AAR-11483 was lost during dating.

The hardwater effect at Schlammersdorf and Kayhude seems to be larger than the effect reported by Fischer and Heinemeier (2003), at least for the fish bones. In their study area, the Amose on Zealand, Denmark, the fish was 100 to 500 14C years older than the archaeological context, while the food crusts were up to 300 14C years older.

**Neustadt** The two outer crust samples from EBK pottery gave very dark solutions under treatment with NaOH. Therefore, the base-soluble fraction was precipitated and dated as well (the method is described in chapter 3). The base-soluble fraction is in this case unlikely to consist of humic substances, as the inner crust samples from the same sherds had much lower concentration of base-soluble substances. Humic substances are a contamination from the burial environment which obviously was the same for two sides of the same sherd.

When compared with the context and with associated food crust samples, lipids from Ertebølle pottery are too old, even though they have indication of dairy, or at least terrestrial animal, fat. Lipids from Funnel Beaker pottery, however, are slightly younger than expected.

In figures 6.36 and 6.35, the calibrated ages of the samples from Kayhude and Schlammersdorf are given, assuming that the terrestrial calibration curve IntCal09 (Reimer et al., 2009) can be used for the calibration of all samples.

**Radiocarbon dates and stable isotope ratios** In figure 6.37, the isotope ratios of experimental food crusts are plotted together with isotope ratios and 14C ages of the radiocarbon dated food crusts from Neustadt, Kayhude and Schlammersdorf.

The samples from Neustadt clearly have a marine component. For comparison, the experimental porpoise crust has $\delta^{13}C = -19.58\%$, (average of DI and EA measurements). A reservoir age of 200-400 years for the Neustadt crusts is suggested.

For the Kayhude samples, the $^{14}C$ age is higher for lower $\delta^{13}C$ values (as low as -28.9%), and higher $\delta^{15}N$. The age of the oldest crust, 6090 uncal BP, is thus assumed to be too high. The youngest crust from Kayhude, with 5350 uncal BP, $\delta^{15}N=6.4\%$, $\delta^{13}C=-26.5\%$, possibly consists of terrestrial material. The calibrated age range for the youngest Kayhude crust is 4440–3960 BC (95.4%, calibrated with OxCal 4.1 and IntCal09). The second youngest is significantly older, 4690–4370 BC (95.4%). Due to the high probability of a freshwater reservoir effect in the oldest food crusts from Kayhude, I conclude that the pottery from this site most likely is younger than 5000 cal. BC. It may be even younger than coastal pottery, which has ages around 4600 cal BC.

The oldest food crust from Schlammersdorf has $\delta^{13}C=-27.2\%$ and $\delta^{15}N=4\%$. This $\delta^{15}N$ value is the highest for all Schlammersdorf food crusts. Compared to the other food crusts in figure 6.37 however, it is relatively low. The crust probably consists of terrestrial material, and the extremely high age of 5500 cal. BC could be correct. However, $\delta^{15}N$ values of food crusts from Schlammersdorf are generally quite low.

In conclusion, both the comparison with dates of the context and with stable isotope ratios indicates the possibility of a freshwater reservoir effect in the food crusts from the inland sites Kayhude and Schlammersdorf, and a marine reservoir effect in the food crusts from the coastal site Neustadt.

**Omitted samples** Some very small samples could not be measured due to problems with the accelerator (table 6.16). These include a plant rest from within a sherd, SID 12347, SLA5-1713, of which two other cathodes had been prepared: C-19979, food crust (14C age 6850±120), and C-19974, outer crust (5190±110). The other two lost samples are a terrestrial bone and a fish bone from Kayhude. Cathodes had been prepared for all three of these samples. As they were all very small, it was decided to wait with the measurement until the ion source and accelerator settings were optimised for very small samples. However, the accelerator was put out of action before this could take place. As a long storage period of the cathodes makes the dating results unreliable because of possible accumulation of modern contamination, it was decided after some time to discard these cathodes.
6.4. RADIOCARBON DATING OF ARCHAEOLOGICAL SAMPLES

Figure 6.33: Uncalibrated radiocarbon ages of archaeological samples from Schlammersdorf/Trave. The plot was made with OxCal 4.1 (Bronk Ramsey, 2009), using a straight line $y=x$ as a “calibration curve”. $2\sigma$-intervals are indicated below the probability distributions of the radiocarbon ages.

Table 6.16: Cathodes of archaeological samples that could not be measured because they had waited too long for the accelerator to work again.
Figure 6.34: Uncalibrated radiocarbon ages of archaeological samples from the coastal site Neusadt. The plot was made with OxCal 4.1 (Bronk Ramsey, 2009), using a straight line y=x as a “calibration curve”. 2σ-intervals are indicated below the probability distributions of the radiocarbon ages. Radiocarbon dates from Craig et al. (2011).
6.4. RADIOCARBON DATING OF ARCHAEOLOGICAL SAMPLES

Figure 6.35: Calibrated ages of archaeological samples from Schlamersdorf/Trave. The plot was made with OxCal 4.1 (Bronk Ramsey, 2009), using the terrestrial calibration curve IntCal09 (Reimer et al., 2009). 2σ-intervals are indicated below the probability distributions of the calibrated ages. Age ranges of fishbones and of terrestrial samples are shaded blue and green, respectively.
Figure 6.36: Calibrated ages of archaeological samples from Kayhude/Alster. The plot was made with OxCal 4.1 (Bronk Ramsey, 2009), using the terrestrial calibration curve IntCal09 (Reimer et al., 2009). 2σ-intervals are indicated below the probability distributions of the calibrated ages. Age ranges of fish bones and of terrestrial samples are shaded blue and green, respectively.

Figure 6.37: Radiocarbon dates of some of the archaeological food crusts from Kayhude, Neustadt and Schlamersdorf on the background of isotope values of food crusts (cf. figure 6.19).
6.5 Additional methods for food crust analysis

This section presents preliminary studies of the suitability of three additional techniques for the analysis of food crusts. All techniques could be tested by measurements on the food crusts produced in the experiments described above. Some archaeological samples were examined as well. Lipid analysis is already an established technique for the analysis of fatty acids from the ceramic sherd. As this implies the destruction of the sherd, I tested lipid analysis on food crusts, which can be removed from the sherd without destroying the pottery. FTIR spectra of numerous reference food crusts were recorded and will form the basis of a reference library for food crust analysis. A few spectra are discussed to exemplify the wealth of information that can be obtained from FTIR spectra. Finally, the observations made with a petrographic microscope on some food crust samples are noted and illustrated with photographs.

6.5.1 Lipid analysis

Dorte Spangsmark and Linda B. Madsen from Aalborg University in Esbjerg measured the fatty acid composition of lipids absorbed in prehistoric pottery (Spangsmark and Madsen, 2005). For this technique, 1-2 g of potsherd are crushed. Chloroform and methanol were used for extracting the fat. After centrifuging, the residue is discarded. The fluid is evaporated and then derivatised: The lipid substances are made into esters so they can be analysed by the GC.

As the potsherds have to be destroyed for these measurements, the most valuable or archaeologically interesting samples would never be analysed. Therefore, we tried to extract lipids from food crusts, as these could be scraped off the ceramics without destroying the sherd. 100-200 mg food crust were treated just like the crushed potsherds. Archaeological food crusts were examined, but also modern food crusts, to test the reliability of the method.

In the beginning, it was not clear whether the method would work with modern food crusts, because for the measurement, the fats must be degraded to fatty acids. The results of the measurements on three archaeological food crusts, one archaeological sherd, and six food crusts from the experiments are given in table 6.17.

The results from the four archaeological samples are inconclusive. This could be a result of advanced degradation of the samples. Four of the six modern samples are identified correctly. Regarding the fact that the GC in Esbjerg had not been optimised for the processing of these sample types, the results are promising. Further research should clearly focus on lipid analysis of food crusts.

Lipid analysis on samples from Neustadt was performed by Craig et al. (2011). They also extracted lipids for me for radiocarbon dating. The results of their lipid analyses will not be discussed here. However, their results will be used to classify the dated lipids. The fatty acids C18:0 and C16:0 are present
Table 6.17: GC analysis of potsherds and food crusts, made in Esbjerg by Dorte Spangsmark and Linda B. Madsen (for abbreviations and methods, see e.g. Ackman and Hooper, 1968; Craig et al., 2007; Spangsmark and Madsen, 2005)

<table>
<thead>
<tr>
<th>SID</th>
<th>Description</th>
<th>What was used?</th>
<th>What was found?</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>12017 arch. (Kay)</td>
<td>food crust</td>
<td>C16/C18 ≤ 1, minimum amounts of FA (C15, C17 or C19), no FA ≥ 20</td>
<td>not fish or ruminant</td>
<td></td>
</tr>
<tr>
<td>12048 arch. (Kay)</td>
<td>food crust</td>
<td>C16/C18 ≤ 1, minimum amounts of FA (C15, C17 or C19), no FA ≥ 20</td>
<td>not fish or ruminant</td>
<td></td>
</tr>
<tr>
<td>12345 arch. (Kay)</td>
<td>food crust</td>
<td>C16/C18 ≤ 1, minimum amounts of FA (C15, C17 or C19), no FA ≥ 20</td>
<td>not fish or ruminant</td>
<td></td>
</tr>
<tr>
<td>SLA5-2721 arch. (Sla)</td>
<td>potsherd</td>
<td>C16/C18 ≤ 1, minimum amounts of FA (C15, C17 or C19), no FA ≥ 20</td>
<td>not fish or ruminant</td>
<td></td>
</tr>
<tr>
<td>13816 exp cooked roach and vegetables</td>
<td></td>
<td>contains cholesterol and C15, C17 and C19</td>
<td>ruminant, but C16/C18 indicates fish</td>
<td></td>
</tr>
<tr>
<td>13869 exp food crust vegetables</td>
<td></td>
<td></td>
<td>no animal fats</td>
<td></td>
</tr>
<tr>
<td>13882 exp food crust cod and vegetables</td>
<td></td>
<td></td>
<td>plants and fish</td>
<td></td>
</tr>
<tr>
<td>13887 exp food crust roach and vegetables</td>
<td></td>
<td></td>
<td>fish</td>
<td></td>
</tr>
<tr>
<td>13891 exp food crust roe deer and vegetables</td>
<td></td>
<td></td>
<td>ruminant and plants</td>
<td></td>
</tr>
<tr>
<td>13894 exp food crust plaice and roe deer</td>
<td></td>
<td></td>
<td>very small amounts of fat, maybe pig or wild boar</td>
<td></td>
</tr>
</tbody>
</table>

in almost all degraded fats and often occur in prehistoric pottery. Several EBK samples are dominated by cholesterol and its degradation products, but contain almost no other fatty acids. The identification is thus difficult. Wax, which could be beeswax or plant wax, was found in a few EBK sherds. Two EBK lamps contained the whole range of aquatic biomolecules, which is consistent with blubber and thus supports the interpretation of these shallow bowls as blubber lamps (e.g. Mathiassen, 1935). The gas chromatographic separation of lipids can be combined with combustion and isotope ratio mass spectrometry of individual fatty acids (GC-C-IRMS) and further distinguish between fat sources. The measured isotope ratios are compared to reference fats. Using this technique, some EBK samples were interpreted to contain dairy fats – which is unrealistic considering that the EBK economy was based on hunting, fishing and gathering. It is possible that the “dairy” fats in reality were roe deer adipose fat. However, it is very difficult to obtain truly “pristine” reference fats.

Contacts of EBK groups with Neolithic cultures are reflected in numerous artefacts that were exchanged. One could therefore also imagine that dairy products or cattle had been exchanged. However, this is pure speculation until more analyses on reference fat have been performed. Roe deer fat from Europe’s last pristine forest in Poland possibly has the same fatty acid isotope ratios as the roe deer in the Ertebølle period, and will be analysed in the future.

Lipid analyses from Neustadt also show that pottery was used for other purposes than preparation and storage of food. This is exemplified by the wax remains from some EBK sherds, but also remains of wood tar in a few TRB samples.

Radiocarbon datings of the lipids extracted from pottery from Neustadt are discussed on page 134.
6.5.2 FTIR spectroscopy of food crusts on pottery

The main purpose of this part of the study was to build up a reference library for food crust analyses. Furthermore, the potential of FTIR spectroscopy for the analysis of prehistoric pottery with food crusts was examined. Spectra of modern experimental food crusts were recorded and compared. The aim was to find peaks or peak height ratios that are characteristic for certain ingredients. As a result of differences in sample sizes, peak heights or transmission percentages cannot be compared directly. Only the relative shape and peak heights can be compared. Transmittance is given in percent and the absorbed frequencies are measured as wave numbers in cm\(^{-1}\). Details on measurement technique, sample preparation and examples for the application of FTIR spectroscopy in archaeological science are given in chapter 2.

The collection of reference spectra, which will form the basis of a reference library, is given in the appendix. In the future, these spectra will be analysed in greater detail and they will be compared to published reference spectra of e.g. food. In the following, some examples for possible analyses of the spectra are given. I will start by comparing some of the spectra with each other, then show some comparisons of my spectra with spectra from the literature.

It has been tried whether similar ingredients give similar spectra. Figure 6.38 displays the FTIR spectra of the raw ingredients. The spectra are very similar, but some differences can be observed in the region between 1000 and 1800 cm\(^{-1}\). All three vegetable samples have high transmittance around 1200 cm\(^{-1}\), whereas the transmittance of the fish and meat samples is decreasing in this region. The absorption between 1350 and 1500 cm\(^{-1}\) is broad for the vegetables but has the form of a double minimum for the meat and fish samples. The large absorption at 3300-3500 cm\(^{-1}\) is deeper for the plants than for the meat and fish, when compared to the rest of the respective spectrum, and has a slightly different shape. In the region 700-1000 cm\(^{-1}\), the spectra of meat and fish are very similar and can easily be distinguished from the plant spectra. The spectra of celery and rocket are here very similar to each other, too. However, the spectrum of chard has a sharp absorption peak at 780 cm\(^{-1}\) which cannot be found in the spectra of the other ingredients.

It has been reported that a high 3012 cm\(^{-1}/2923\) cm\(^{-1}\) peak ratio indicates higher concentrations of polyunsaturated fatty acids such as EPA (Eicosapentaenoic acid) and DHA (Docosahexaenoic acid) which are omega-3 fatty acids and characteristic of oily fish (Zhang, 2009). In the spectra of the ingredients, no such pair of peaks has been identified (Figure 6.38). However, there are pairs of peaks at 2957 cm\(^{-1}/2922\) cm\(^{-1}\). The absorption at 3012 cm\(^{-1}\) (Zhang, 2009) might be shifted to lower wave numbers when entire flesh samples are analysed instead of pure oils. The ratio of the absorptions at 2957 cm\(^{-1}/2922\) cm\(^{-1}\) is largest for cod and plaice (about 1) and significantly lower for the other ingredients, including roach, roe deer meat and the vegetables. The absorption at 2957 cm\(^{-1}\) cannot be found in the celery spectrum.

In conclusion, FTIR spectra can distinguish raw plant food from raw meat and fish. Furthermore, marine fish can be identified. However, the spectra of freshwater fish and terrestrial meat are too similar to allow a distinction.

Figures 6.39, 6.40 and 6.41 exemplify how FTIR spectra of ingredients can change when they are cooked together with other ingredients and charred. The 2957 cm\(^{-1}/2922\) cm\(^{-1}\) ratio of the cod becomes smaller when it is cooked and charred with vegetables. However, in one crust, the original ratio is preserved, presumably because a piece of cod charred at this spot of the vessel surface. This is thus a signature that potentially is preserved after charring. Raw and cooked cod are very similar. Only the peak between 1500 and 1250 cm\(^{-1}\) becomes smaller.

An absorption around 750 cm\(^{-1}\) can not be found in vegetables and some mixtures, but occurs in experimental wild boar food crust and roach food crust. An absorption around 778 cm\(^{-1}\), in contrast, can only be found in vegetables or in mixtures that contain vegetables (and one fish that had been cooked together with vegetables). These absorptions might thus be characteristic for fish/meat and for vegetables, respectively.

There is one absorption in the region between 551 and 562 cm\(^{-1}\) which only occurs in cooked or charred samples (and in two archaeological samples), but not in raw ingredients. Most of the samples with an absorption in this region contain fish, although also a vegetable crust and roe deer meat (that had been cooked together with plaice) belong to this group. This absorption probably reflects molecular changes during heating.

As an example for comparison of pre-treated and not pre-treated food crusts, I show the spectra of SID 12047 and SID 12048, two food crusts from the archaeological site Kayhude. The pre-treatment procedure, acid-base-acid, is described in chapter 3. For SID 12047, the pre-treated and not pre-treated samples have similar spectra, but differences at lower wave numbers. The unpretreated food crust has peaks at 1374 and 1025, the pretreated only one broad peak.
CHAPTER 6. FRESHWATER EFFECT IN NORTHERN GERMANY

Figure 6.38: FTIR spectra of ingredients for food crust experiments

Figure 6.39: FTIR spectrum of raw, cooked and charred roe deer meat. In one experiment, the roe deer meat was cooked together with vegetables, in the other together with plaice. Note that the x-axis is in reverse order, compared to the other spectra.
6.5. ADDITIONAL METHODS FOR FOOD CRUST ANALYSIS

Figure 6.40: FTIR spectrum of raw, cooked and charred roach (freshwater fish). The roach was cooked together with vegetables.

at 1213. Furthermore, the unpretreated food crust has two pronounced peaks at 602 and 551 cm$^{-1}$, whereas the pre-treated does not have any peaks in that region.

The position and height of some peaks only change slightly under pre-treatment. For 12048, 465 cm$^{-1}$ changes from being a peak to being a shoulder; 778 cm$^{-1}$ to 763 cm$^{-1}$; 1032 cm$^{-1}$ from peak to shoulder; a large peak at 1374 cm$^{-1}$ to a small peak at 1370 cm$^{-1}$, 1588 cm$^{-1}$ to 1586 cm$^{-1}$. In food crust SID 12047, the peaks at 750 cm$^{-1}$ and 1600 cm$^{-1}$ remain unchanged. Some peaks occur only in the unpretreated samples, like 551/552 cm$^{-1}$ and 602/600 cm$^{-1}$. Some peaks occur only in the pretreated samples, like 1213/1219 cm$^{-1}$. For SID 12047, the pretreatment removes the peaks at 602 and 551 cm$^{-1}$ without replacing them and removes the doublet 1025/1075 cm$^{-1}$ and the peak 1374 cm$^{-1}$ and replaces them with a peak at 1213 cm$^{-1}$. For SID 12048, pretreatment removes the peaks at 552 and 600 cm$^{-1}$ without replacing them. The doublet 1032/1089 cm$^{-1}$ and the peak 1374 cm$^{-1}$ are replaced by a peak at 1219 cm$^{-1}$ with shoulders at 1034 cm$^{-1}$ and 1370 cm$^{-1}$.

Certain peaks seem thus to be characteristic for some of the substances that are removed from the samples during pre-treatment. Future studies could analyse samples between different steps of the pre-treatment procedure. The FTIR spectrum of a food crust might in the future also be used for assessing the degree of preservation of the food crust, or for planning a pre-treatment procedure adapted to that specific sample.

An archaeological food crust from the coastal site Neustadt is compared to different experimental food crusts in figure 6.44. Stable isotope measurement of this food crust indicates that it contains marine fish. It is difficult to decide which of the spectra are most similar. Around 3000 cm$^{-1}$ and 1500 cm$^{-1}$, the most similar spectrum is that of the cod and vegetables crust. However, at lower wave numbers, similarities with other spectra are greater. An identification of the Neustadt food crust from its FTIR spectrum is thus not possible yet.

The food crust made from wild boar meat is compared to two spectra from the literature. As the wild boar food crust dissolved completely in NaOH, the base-soluble fraction was used. It is termed “humic”, as NaOH treatment often dissolves humic substances during the pre-treatment of archaeological samples.
The wild boar food crust has never been buried in soil, and thus does not contain any humic substances. Instead, the base soluble fraction is believed to contain significant amounts of fat. In figure 6.45, it is compared to a spectrum of pork fat (Flätten et al., 2005). The spectra agree nicely, apart from the region between 1700 and 1600 cm\(^{-1}\). However, figure 6.46 illustrates that spectra of fat and oil in general are very similar (spectrum from Guillén and Cabo, 1997). A more thorough analysis should thus take the precise wave numbers of the absorptions and their relative heights into account.

In conclusion, an extensive reference library of food crusts on pottery has been built up. The complexity of FTIR analysis was demonstrated. Further analyses will include focus on specific absorptions, instead of comparing whole spectra, as well as computer-aided analysis.

### 6.5.3 Petrographic microscopy

Petrographic microscopy may identify numerous interesting substances in food crusts on pottery, as summarized shortly in section 2.4.5. It was for example used to identify phytoliths in food remains on Ertebolle ceramics (Arrhenius and Liding, 1989). I have therefore tried to apply this technique to food crusts on pottery. The observations I made on some experimental and archaeological samples are given in table 6.18. I would not have been able to do these interpretations on my own and could fortunately benefit from the expertise of Elisabetta Boaretto, Erik Thomsen and Hans Dieter Zimmermann.

#### Sample preparation

SID 12048a, 12345a, 12350a+b (see table 6.18 for information about the samples) were put directly onto the microscope slide, and there, they were pulverised with a spatula in a drop of water. 12350a is coarse and probably contains a lot of clay, 12350b is finer and darker. SID 12048b and 12345b were pulverised in water in test tubes. It has been tried for SID 12048 whether it is possible to pulverise the sample in an ultrasonic bath, but that is not the case. Crushing the samples in test tubes instead of crushing them on the slides does not make better samples, but some material can be lost. Thus, all the other samples were just pulverised directly on the slides in a drop of water. They were then dried under the desk lamp. After
drying, etc. remaining large particles were removed by scraping or tapping. A drop of silicone oil was put onto the sample which was then covered by the cover slip. Colourless nail polish was used to seal the edges of the cover slip while avoiding the trapping of air bubbles. Scans of the slides and photographs of the microscope image will be presented in chapter 6.

**Observations**

Unfortunately, no organic material could be discerned. Apart from some occasional clay or charcoal particles, no indications for the origin of a food crust could be identified. Neither could information about the presence of contaminants or the preservation of the food crusts be obtained.

Figures 6.47, 6.48, 6.49 and 6.50 show examples for petrographic microscopy of food crusts. Each sample was also scanned twice, one of the scans including crossed polarisation filters. Figures 6.51 and 6.52 show examples of such scans.
Figure 6.43: Food crust pre-treatment: FTIR spectrum of SID 12048.
Figure 6.44: Comparison of FTIR spectra of an archaeological food crust from the coastal site Neustadt and different experimental food crusts.
Figure 6.45: Comparison of FTIR spectra of experimental wild boar food crust (two samples, base soluble fraction) and pork fat (Flätten et al., 2005).
6.5. ADDITIONAL METHODS FOR FOOD CRUST ANALYSIS

Figure 6.46: Comparison of FTIR spectra of experimental wild boar food crust (two samples, base soluble fraction) and lard and different edible oils (Guillén and Cabo, 1997)
Table 6.18: Petrographic microscopy of food crusts. The observations noted in italics were made with the help of Elisabetta Boaretto during the Tell es-Safi/Gath Archaeological Science Field School (organised by Bar Ilan University and Weizmann Institute). The other observations were made at the Department of Geoscience, Aarhus University, with the help of Erik Thomsen and Hans Dieter Zimmermann. For some observations, the magnification is given (indicated by x and the number).

<table>
<thead>
<tr>
<th>AAR-number, sample ID (SID), sample name and additional information</th>
<th>Observations during petrographic microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AAR-11409</strong>, SID 12053, N-629, Neustadt, coastal site.</td>
<td>No phytoliths. With crossed polarisation filters: some brown, clear and coloured spots, no forams, an elongated object, about 1/4mm long, 25-40um wide; the others a bit smaller. With crossed and non-crossed filters: red elongated object 10-20um wide and 1.5mm long. Brown particles: clay.</td>
</tr>
<tr>
<td><strong>AAR-11403</strong>, SID 12047</td>
<td>Only black and clear spots; a lot of charcoal in different sizes, very small particles. With crossed filters, there are only structureless bright parts, no forams, no phytoliths, but an elongated object. Mainly black particles, few are brown with crossed filters, the sample is completely dark with crossed filters apart from few tiny pieces which probably are quartz. Almost exclusively black particles, also some brown particles, which also become dark when the polarisation filter is turned. What looked like big, sharp-edged quartz particles with the modern samples (see below) could in reality be pieces of cellulose (with a few of them, we could see the structure). This also seems to occur in the archaeological sample, but fewer and smaller.</td>
</tr>
<tr>
<td><strong>AAR-11484</strong>, SID 12350, SLA5-1802a</td>
<td>Sponge spicula, one foraminifer (oval with cross), several diatoms. Oxalate (slightly elongated hexagonal form) from firewood?, one huge phytolith and a smaller one. Some big charcoal pieces.</td>
</tr>
<tr>
<td>SID 12350b</td>
<td>256x: Many brown essentially structureless particles, might be clay. There is one particle which is black, but lights up strongly, this must be a mineral, but it is hard to see, which mineral, maybe it is chalk.</td>
</tr>
<tr>
<td>SID 12350a</td>
<td>1.6x16x10: Several particles are colourless to brownish in parallel polarised light. Some of the show blue-green interference colours when the upper filter is inserted, but not crossed. In crossed filters, these particles light up strongly. However, they could not be identified. There are some totally black particles which might be pyrite from the clay or granite.</td>
</tr>
<tr>
<td>Cod and vegetables</td>
<td>red, with inner structure, which shines red with crossed filters: plant.</td>
</tr>
</tbody>
</table>

Continued on next page
### 6.5. **ADDITIONAL METHODS FOR FOOD CRUST ANALYSIS**

<table>
<thead>
<tr>
<th>AAR-no., SID, name</th>
<th>Observations during petrographic microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SID 12048</td>
<td>small totally black particles, several small quartz pieces, several small particles which light up red/brown with crossed filters, brownish organic particles. 256x: several brown particles do not light up, some particles have no inner structure, some others have an inner structure which is not ordered and those particles only light up slightly (also they are brown). 400x: a fibrous brownish particle lights up but changes intensity when rotating.</td>
</tr>
<tr>
<td>SID 12048a</td>
<td>grain 1 can well be an aggregate of two grains; I took a photograph of the lower one (this is the first picture of 12048a); in the lower magnifications, nothing else could be seen. Grain 2: cell structure. Grain 4: very little double refraction and very little anisotropy.</td>
</tr>
<tr>
<td>SID 12345a</td>
<td>one long reddish fibre that lights up: probably modern contamination (clothes, dust, hair). The black particles are a bit larger than for the last sample (SID 12048), there is no quartz, but it seems as if there are more of the brown particles, some with an inner structure that partly lights up when rotating (6x1.6x10). 400x: there are brown particles without inner structure that do not light up and some with an inner structure that lights up partly when rotating, it must be something organic with inorganic inclusions.</td>
</tr>
<tr>
<td>SID 12345b</td>
<td>mainly structureless black particles, in between a few brown and colourless particles. The brown particles have a granular, not ordered structure in 40x magnification. Single particles are red-brown and more homogeneous.</td>
</tr>
<tr>
<td>SID 13894b</td>
<td>one crystal in extinction position when the parallel stripes are in north-south direction; the brown particles are not crystals. In all three grains, the parallel lines are parallel with the length direction. The brown spots are maybe iron oxide. Iron can oxidise at 800°C. Iron(II) from plant material could probably oxidise with lower temperatures; it might be hematite that was formed from the iron of the clay. The lighter brown particles could be very thin haematite sheets which still are a slightly translucent.</td>
</tr>
</tbody>
</table>
Figure 6.47: Polarisation microscopy of food crust sample SID 12048b. ppl: parallel polarized light; xpl: crossed polarisation filters; the $\lambda$ plate shifts the light with 550 nm.
6.5. ADDITIONAL METHODS FOR FOOD CRUST ANALYSIS

Figure 6.48: Polarisation microscopy of food crust sample SID 12345a, ppl: parallel polarized light; xpl: crossed polarisation filters; the $\lambda$ plate shifts the light with 550 nm.
Figure 6.49: Polarisation microscopy of food crust sample SID 12345b. ppl: parallel polarized light; xpl: crossed polarisation filters; the λ plate shifts the light with 550 nm.
6.5. ADDITIONAL METHODS FOR FOOD CRUST ANALYSIS

Figure 6.50: Polarisation microscopy of food crust sample SID 12350a. ppl: parallel polarized light; xpl: crossed polarisation filters; the λ plate shifts the light with 550 nm.
CHAPTER 6. FRESHWATER EFFECT IN NORTHERN GERMANY

Figure 6.51: Scans of food crust sample SID 13882 (two slides: 13882a and 13882b). ppl: parallel polarized light; xpl: crossed polarisation filters.

Figure 6.52: Scans of food crust sample SID 13894 (two slides: 13894a and 13894b). ppl: parallel polarized light; xpl: crossed polarisation filters.
6.6 Conclusion

The freshwater reservoir effect in the rivers Alster and Trave is large and very variable. In both rivers, $^{14}$C age and $\delta^{13}$C values of water DIC are correlated. The origin of the water thus explains its age. The more dissolved old carbonate in the water, the higher the $\delta^{13}$C values, as the ancient marine carbonates have $\delta^{13}$C$\approx$0, and the higher the $^{14}$C ages, as the ancient limestones do not longer contain any $^{14}$C. Furthermore, $\delta^{13}$C and $^{14}$C of water DIC are correlated with the amount of precipitation during the week before sampling. The high variability of the $^{14}$C ages can thus be explained with short-term fluctuations in precipitation. In periods with high precipitation, terrestrial run-off with CO$_2$ from the root zone ($\delta^{13}$C$\approx$25$\%\textsubscript{o}$, recent $^{14}$C levels) becomes relatively more important in the rivers, in contrast to the more or less constant supply of groundwater with dissolved old carbonate.

The high ages and great variability can also be found in aquatic plants. Short-term fluctuations in precipitation are unlikely the reason, as the plants average $^{14}$C levels over the entire growth season. Aquatic plants can utilise a multitude of carbon species for photosynthesis: HCO$_3^-$ or CO$_2$ in the water (DIC), atmospheric CO$_2$ in the case of emergent or floating species, and CO$_2$ from decaying organic material at the bottom of the river in case of rooted species. Some aquatic plants can store nutrients from the previous growth seasons for the growth in early spring. The DIC species can have high apparent ages, but also the other carbon sources have different $^{14}$C ages. The “true” age of the organic material stored in a plant’s rhizome or at the bottom of the rivers can be several years, and this would lead to much higher differences in radiocarbon age, due to the bomb pulse (see section 2.1.3). The high reservoir age of floating leaves clearly shows that the assimilation of atmospheric CO$_2$ is not the dominant carbon source for these specimens, despite the expectations. This result is clearly interesting for freshwater botanists. Radiocarbon dating might in the future be used for identifying carbon sources in photosynthesis of aquatic plants in their natural environment, as long as this is an aquatic system with high water DIC ages.

It is striking that, in spite of the influence of bomb carbon, almost all modern river samples have high $^{14}$C ages. This indicates a substantial reservoir effect which would be even greater without the bomb effect.

Cooking experiments and analyses of the experimental food crusts have proven that a high reservoir effect of the ingredients is transferred to the food crust. Stable isotope analysis of food crusts from a small potsherd cannot identify the precise recipe, if a mixture of ingredients had been cooked. This is due to the fact that different lumps of food char at different places in the pot. Stable isotope analysis of food residues of single sherds can thus not be used to reconstruct palaeodiet or palaeocuisine. However, they can indicate the possibility of freshwater or marine food, and thus a reservoir effect in the food crust analysed.

Lipids can be extracted from both potsherds and from food crusts. The analysis of fatty acids extracted from food crusts, however, needs to be optimized. Lipids can also be extracted in sufficient quantities for radiocarbon dating. Some lipid dates are certainly too old, although the residues were purely terrestrial. Reservoir effects were therefore not indicated. However, the contamination with old carbon from the clay or from chemicals used during sample extraction is unlikely, as the trend to higher ages is not systematic, and some lipids were actually younger than expected from their archaeological context. Further research will focus on radiocarbon dating of single fatty acids and improve the extraction methods to eliminate possible sources of contamination. The mysterious presence of dairy fat in a hunter-fisher-gatherer culture will be examined more closely and hopefully solve the riddle of milk products in the Mesolithic.

The archaeological material as well indicates a substantial freshwater reservoir effect, although we can be less certain, as we do not know the true age of the archaeological food crusts or aquatic samples. We can assume the youngest food crusts to show the true age of the pottery, while the older crusts are affected by a reservoir effect. The large spread of terrestrial ages shows the unclear stratigraphic situation and emphasizes the importance of direct pottery dating.

The reservoir effect in the two rivers could have been higher during the Stone Age, as one could assume that a lot of the carbonate present in the underground of the rivers has leached out since then. The concentration of old carbonate in the rivers could thus have been higher during the Stone Age. However, as the rivers were broader, more shallow, more meandering and slower running, more atmospheric exchange could have taken place. The age difference between archaeological fish bones and terrestrial samples indicates the reservoir effect in the Stone Age, if we assume that these samples were contemporaneous. In the Trave, the reservoir age is more than 1000 years, in the Alster, almost 3000 years.

Both for modern and archaeological samples, the reservoir age in the Alster is higher than in the Trave. Water hardness and cation ratios in the rivers would lead to the opposite expectation. This indicates that...
dissolved carbonate minerals are not the only source for the high reservoir ages. Mineralized organic matter or groundwater with high “real” ages could have increased the reservoir age of Alster water, while exchange with the atmosphere could have decreased the reservoir age in the Trave while it passed the shallow Wardersee.

In general, this study shows that the characterization of the reservoir effect in a freshwater system requires more than a few water-, plant or animal samples. It is shown that freshwater reservoir effects in rivers can be very high and strongly variable. Archaeologists should be made aware of this source of spurious ages when sending pottery or bones of omnivores like humans from inland sites for 14C dating.

The surprisingly high ages of Northern German pottery are in all likelihood caused by the freshwater reservoir effect. There is no longer reason to believe that inland potters were hundreds of years ahead of their colleagues at the coast.
Chapter 7

The Limfjord

While the previous chapter on Northern Germany examined moments in time, the Mesolithic and today, we will follow the development of the Limfjord for a long period of time by examining a sediment core. In the last chapter, we have seen how large the freshwater reservoir effect variability is for one river during few years. Here, we will have a look at samples that accumulated over longer periods of time and not represent single water plants, to see if the short-term fluctuations equalize. Many of the cultural and environmental developments and technical terms mentioned here are explained in chapter 5. Stable isotopes of bulk sediment will be measured to trace the source of the organic matter. These measurements are part of a multi-proxy study, and my results will be discussed along with results from the other methods (Lewis et al., submitted; Philippsen et al., submitted).

7.1 Introduction

Estuaries generally sustain high organic productivity and biological diversity, making them attractive habitation areas for humans in prehistoric as well as historic time (Clark, 1983; Andersen, 2007). The Limfjord in northern Jutland, Denmark is an example of such an environment (Baudou, 1985; Davidsen, 1985; Hedeager, 1985; Kristiansen, 1985; Vandkilde, 1990; Mathiassen, 1948). Settlements along the Limfjord coast have had easy access to rich resources such as marine and freshwater fish, shellfish, and marine mammals. The salinity of brackish, partly enclosed seas with small tidal ranges, like the Kattegat and the Limfjord, depends on the degree of connection to the fully saline ocean, in this case the North Sea. The resources available at different periods have thus varied according to the palaeoenvironment. It has long been recognized that the Limfjord is a variable environment, with varying connections to the sea and varying salinity (e.g. Jørgensen, 1870).

While estuaries are favourable as settlement locations, they are problematic for the radiocarbon analyst. Fjords and estuaries pose the challenge of site and time specific radiocarbon reservoir ages due to the mixture of fresh and marine waters, thus a mixture of marine and freshwater reservoir effects (section 2.1.4; e.g. Heier-Nielsen et al., 1995; Olsen et al., 2009).

The timing and positioning of openings from the Limfjord to the open sea, especially during the Viking Age, has been debated for the last 150 years (Christensen et al., 2004; Andresen, 1856; Jørgensen, 1870; Steenstrup, 1875; Bricka, 1869; Petersen, 1976; Erskle, 1873; Kristensen et al., 1995; Bricka, 1871). However, there has been a lack of long records with good chronological control of the environmental development of the Limfjord (Andersen, 1992a; Petersen, 1985a). Radiocarbon dates for environmental and archaeological studies were often made on marine material alone (e.g. Andersen, 1993; Christensen et al., 2004).

Here the reservoir age variability and environmental history of the south-western part of the Limfjord is presented. The multi-proxy approach includes study of sedimentary micro- and macrofossils, geochemistry (organic matter content, C/N ratios), stable isotopes of sediment organic matter ($\delta^{13}C$, $\delta^{15}N$) and radiocarbon reservoir ages to infer past changes in organic matter origin, nutrient source, salinity and $^{14}C$ reservoir ages in the context of archaeological evidence. Before presenting my own measurements, I start with a review of the work on the Limfjord performed during the last 150 years.

7.2 Development of the Limfjord

This account is ordered chronologically, from the formation of the Limfjord after the last glacial period towards the present. It is divided into phases according to the cultural development in Denmark, from
the Stone Age until historical times (see chapter 5 for definitions and datings of these phases).

After the glacial period, there were lakes and rivers in the area of the Limfjord. Then, seawater entered this area, and a marine environment with many islands was formed (Andersen, 1990).

In 13050 BC (15000 cal BP), marine waters reached the Skagen area (Knudsen, 1994). From 11550 to 11050 BC (13500-13000 cal BP), the Kattegat was inundated (Petersen, 1985b). The modern circulation system in the Kattegat and Skagerrak was established around 6550 BC (8500 cal BP) (Gyllencreutz, 2005). The presence of human groups in the Limfjord region is indicated by artefacts made of reindeer antler and the so-called Lyngby arrowheads, belonging to the Bromme culture (cf. chapter 5 Mathiassen, 1948).

It is debated when exactly the Limfjord was formed, and different models have been presented. The formation of the Limfjord was linked to the initial Littorina transgression between 6550 and 6150 BC (8500-8100 cal BP), when the Limfjord was connected to the Skagerrak (Petersen, 1981). This transgression began between 6700 and 6400 BC (8650-8350 cal BP) and marks the transition from Maglemose to Kongemose culture (Christensen, 1995). Different datings were also proposed, between 6000 and 5500 BC (7950-7450 cal BP) Andersen, 1990) or around 7000-6700 BC ((8950-8560 cal BP) Andersen, 1992b).

For a precise dating of the formation of the Limfjord, one would need a well-dated sedimental record spanning both the freshwater period and the early marine period. Unfortunately, no such records are yet available. Marine material like mollusc shells in sediment cores or the archaeological record as well as clearly discernible inundations such as drowned sediment cores or the archaeological record as well as marine period. Unfortunately, no such records are yet available. Marine material like mollusc shells in sediment cores or the archaeological record as well as clearly discernible inundations such as drowned sediments gives a terminus ante quem for the formation of the Limfjord. A terminus ante quem is the latest time at which an event must have happened. The terminus ante quos for the starting of marine influence in different parts of the Limfjord are the following: Heier-Nielsen (1992) 14C-dated marine molluscs from Legrestrial Bredning. The two oldest samples have calibrated ages between ca. 8700 and 7100 cal BC, ca. 10700-9100 cal BP (95.4%), after my calibration with OxCal 4.1 and the marine calibration curve Marine09 (Reimer et al., 2009; Bronk Ramsey, 2009). An oyster bank at Gjøttrup have, Ullerup Gaard, northern-central Limfjord, was dated to 6060-5670 BC (8010-7620 cal BP). On the southern coast of Livø in the central Limfjord, the oldest marine gyttje is from 5620-5210 BC (7570-7160 cal BP). The drowning of the earliest settlement at the Limfjord in 5600 BC (7550 cal BP) (Andersen, 1990) gives a terminus ante quem for the beginning of marine influence in the area – in 5600 BC at the latest the sea must have entered the area in order to flood the settlement. The oldest samples analysed in this study are from ca. 7300 cal BP (5350 BC), thus from a period where all authors agree on the existence of the Limfjord as a marine environment.

It is also debated how fast the sea level rise was that formed the Limfjord. Petersen (1981) suggests 3-4 m per 100 a, according to a drilling at Vust north of the Limfjord, while Christensen (2001) found 1m/100a for the Danish seas. The fast sea level rise at Vust might only be a local phenomenon.

From ca. 5500 BC, 7500 cal BP, the global eustatic sea level rise slowed down, so that regressions or standstills occasionally occurred due to the isostatic uplift of Northern Denmark (Christensen et al., 2004). The resulting fluctuations in relative sea level caused the Limfjord to vary between a marine archipelago and a brackish estuary. The earliest marine maximum was around 5300 BC (7250 cal BP) in the north-northeast and around 4600 BC (6550 cal BP) in the southwestern parts of the Limfjord (Andersen, 1990). The maximum extent of the Sea is shown in figure 5.1 in chapter 5. In the Stone Age, the eastern Limfjord consisted of very large shallow broads, through which the narrow and deep underwater valley “Langerak” went. The eastern Limfjord was only open towards the Kattegatt and at the same time more protected against the open sea by the hills of Himmerland and Vendyssel, resulting in brackish salinities. The western Limfjord was under stronger marine influence and consisted of large and deeper waters, with openings toward the north to the Skagerrak. Only at the narrow Aggersund, the two parts of the Limfjord had been connected (Andersen, 1992b, see also figure 7.2).

Mesolithic There is some uncertainty about the Danish marine environment, including the Limfjord, in the Mesolithic. Iversen (1967a) claims it was warmer, saltier and more nutritious than now and the tidal range was larger. Sea level rise is after his opinion not the only reason for the sudden rise in salinity of the Baltic in the beginning of “Littorina time”. The higher tides were also responsible for the higher salinity. Also Noe-Nygård and Hede (2006) report a strong tidal amplitude of the order of 4 m for the North Sea and Kattegatt during the Atlantic. They are objected by Christensen (1995) who asserts that there is no significant difference in tidal range; his investigations showed that “tides in the Atlantic period were not significantly greater than today”.

However, there is general agreement that the sea level in the Stone Age Limfjord was higher than
today, at least 3 m above the present-day Danish Vertical Reference, DVR90 (Petersen, 1976). In contrast, the proportion of shallow areas in the Limfjord was larger than today, as large areas which now are dry land were shallow bays. Hence, sunlight reached larger areas of the sea floor than today (Andersen, 1992b, 1995). This provided excellent possibilities for photosynthesis and resulted in a much richer flora and fauna. The preconditions for human subsistence were thus particularly advantageous, in an environment that already was favourable due to its estuarine character.

A high salinity in the Stone Age is exemplified by finds from the Ertebølle locus classicus on the central Limfjord. Fishbones of Pollachius indicate high salinity (Enghoff, 1986), as well as the foraminifer Elphidium margaritaceum, which needs a salinity of >30 PSU (Burman and Schmitz, 2005). From isotope measurements (δ13C, δ18O) on periwinkles, the mid-Holocene winter salinity at Ertebølle was calculated to be 31±1 PSU, comparable to the salinity of the present-day North Sea (Burman and Schmitz, 2005).

The productivity of the marine environment was greater in the Stone Age than today. Petersen (1922) calculated that the accumulation of the kitchen midden of Meilgård (northern Djursland, east coast of Jutland) must have taken 1200 years. His calculation was based on modern oyster production. 14C datings, however, showed that the accumulation of Meilgård only took 400-500 years. The biological productivity of the sea decreased thus significantly from the Stone Age to recent times (Andersen, 2001). Also in the Limfjord, high salinity and temperature as well as the shallowness of the water were the basis for high marine productivity (see above and e.g. Andersen, 1995).

These rich resources were exploited by the Stone Age population at the Limfjord. This is proven by numerous remains of Mesolithic coastal sites. In fact, inland sites from this period have not been found in the Limfjord region. All sites are coastal settlements along the former coast. They are relatively easily found in the Limfjord region: the isostatic land rise was larger than the eustatic sea level rise after the end of the glacial period, so that the settlements are not inundated (as is the case for the “southern half” of Denmark and for Northern Germany, see chapter 5). The oldest known settlement on the Limfjord, belonging to the Kongemose Culture, was inundated around 5600 BC (7550 cal BP, Andersen, 1990). Also the oldest kitchen middens are found in the Limfjord area and dated to around 5400 cal BC (7350 cal BP, Andersen, 1995), with my own calibration using OxCal 4.0 and IntCal04. The kitchen midden site Ertebølle was frequented for almost 1000 years, indicating a high degree of resource stability (Andersen, 1992b).

δ13C analyses of human bones as well as artefacts and faunal remains such as fishbones, fishtraps and fish food crusts on pottery indicate that marine resources were the main economic basis of the Mesolithic society (Andersen, 1995, 1993; Andersen and Malmros, 1984). An argument for the importance of hunting marine mammals are specialized tools like the harpoon and the EBK-blubber lamp (Andersen, 1992b). Fishing was mainly performed using permanent structures like weirs and traps. Remains from coastal sites give “a non-selective sample of whatever fish was present in the local coastal waters during the summer half of the year” (Enghoff, 1995). However, coastal settlements where subsistence depended exclusively on the sea have not been found yet (Andersen, 1993). In fact, two kitchen-midden sites from the Limfjord are famous for freshwater fishing: In Ertebølle and Bjernsholm, fishing concentrated on eel (Andersen, 1993). People staying at Ertebølle fished in a nearby freshwater lake, mainly in late summer and autumn (Enghoff, 1995).

Neolithic Although the Stone Age Sea around 3000 BC with its highest sea level opened the fjord to the sea between Hansholm and Svinклов, Nissum Bredning was closed to the west (Meessenburg, 1981). The passage between the Skagerrak and the Limfjord was deepest in the Middle Atlantic, though. The marine influence originating from the connection to the Skagerrak was largest in the Atlantic and decreased during the Subboreal, when beach walls formed in this area (Petersen, 1992).

With the beginning of the Neolithic, kitchen middens and coastal sites became fewer and smaller. Oysters became smaller and were replaced by cockles in the kitchen middens. This has been connected to lowered tidal ranges and lower salinity. Marine mammals were still hunted in the Limfjord area in the Neolithic. In the middle Neolithic, shell middens are again dominated by oysters, but the shell layers are still very thin (Andersen, 1992b).

In spite of the apparent decline in marine resources, there were still natural oyster banks in the Limfjord. There is also evidence for collection of marine shells, and hunting of marine mammals on the coast of the Limfjord (Andersen, 1990, 1992b; Marseen, 1962).

Bronze Age and Iron Age In the Bronze Age, there is a general lack of shell middens in Denmark, while they are numerous before and after, i.e. in the Neolithic and in the Iron Age (Milner et al., 2007). However, the collection of marine mollusks had not ceased
totally, and also fishing in the Limfjord was still important, as the exemplified by the sites Torslev, Vagdågård and Fragtrup (Johansen, 1985; Lomborg, 1973; Draiby, 1985).

During the Iron Age, the salinity in the Baltic was significantly higher than today, which is indicated by large oysters growing in relatively enclosed areas like the Flensborg Fjord or the Bay of Eckernförde (Anger, 1974). During the Stone Age, however, conditions for oysters had been even more favourable. From the early Roman Iron Age on (AD 0-200), the Limfjord began to look like it is today, although there still was a passage from the Skagerrak into the Limfjord. In the late Iron Age, the Limfjord was an important starting point for voyages towards the west (Andersen, 1990). The filling of a pit house on Fur contained marine shells from ca. AD 900, which indicates marine conditions in the Limfjord.

From AD 1000 In AD 1027, an open connection at Agger Tange is known to have existed as the Danish Viking King Knud the Great returned from his expedition to England via this sound (e.g. Petersen, 1976; Kristensen et al., 1995). During the reign of Canute IV of Denmark, AD 1042-1086, there was a free passage from the Limfjord to the North Sea, according to the 11th book of Saxo’s *Gesta danorum*, but this passage was already closed during the time this book of *Gesta danorum* was written (around AD 1200, Bricka, 1869, 1871). However, the state of the Limfjord in the 11th century AD was debated passionately around AD 1870 in the Danish journal *Aarbøger for Nordisk Oldkyndighed og Historie*. A saga accredited to the Icelandic politician, historian and poet Snorre Sturluson (The Sagas of Olaf Tryggvason and of Harald The Tyrant (Harald Haardraade)) tells how the Norwegian King Harald Haardraade fled from a superior Danish fleet lead by King Svend Estridsson in AD 1061 from the Limfjord to the North Sea by emptying his boats, dragging them over a barrier and re-loading them, all during one single night. The debate focused on the question where this barrier had been located. It was suggested that it was a barrier at Agger Tange (Andresen, 1856; Jørgensen, 1870), while others argued that the Limfjord had been widely open at Agger, and Harald transported the ships over the shallows at Løgstør, “Løgstør grunde” (Steenstrup, 1875; Bricka, 1869) or over a small strip of land at Vust (Erslev, 1873) between the Limfjord and the Skagerrak. The question about the interpretation of the saga thus led to a research question which is similar to the question examined in this study: to what extent did the Limfjord have connections with the open sea?

Later research continued to examine this question. It was suggested that Nissum Bredning never had a direct connection to the sea in prehistory, according to the analysis of prehistoric shells and the lack of beach walls of North Sea type in that area (Jessen, 1920). Petersen (1976) suggests that Harald Haardraade fled towards north through a connection from Logstør Bredning to the Skagerrak. Through the Han Herredene region, there are two possibilities for passages to the north: west of Fjerritslev and at Bulbjerg, where there are valleys in the old limestone surface which are now covered by later sediments. On old maps, you can for example follow a trough from the dunes in the north through Klim Odde and Gttrup Rimme and from here, further towards south-east through the coastal meadows to the Limfjord at Ullerup, close to Aggersborg (Møller, 1986). This view is also supported by drillings in the area were the former connection was expected (Petersen, 1976). A chronicle from AD 1186/87 mentions that Humle, most probably Humlum close to Oddesund, was a sea harbour (Aagesen, 1186/1187).

During the following centuries, historical records become more reliable. In AD 1624, “the great breakthrough” happened in the western Limfjord, resulting in a connection to the North Sea for a longer period 7. This connection was near Harboøre and silted up later (Hylleberg, 1992; Andresen, 1856). Until AD 1671, Agger Tange was covered with fields and meadows. After this date, they were ruined by sand entrainment and floods from the North Sea (Andresen, 1856). In the late 18th century, the Limfjord contained “brackish or half salty” water, although it often was more saline when the North Sea under a storm broke through at Agger, or when the inlet at Hals in the east was flooded (Pontoppidan, 1769). In the Middle Ages and up to 1825, the salinity of the Limfjord was %, like today the Baltic Sea around Bornholm (Hylleberg, 1992). The Limfjord was an important fresh- and brackish water fishery (Petersen, 1992) in this period.

On the third February 1825, a flood opened a passage at Agger Tange, turning the Limfjord into a sound (Andresen, 1856). Ships could pass this channel from 1834, so the marine transport was improved, while the road over Agger Tange was damaged. The higher salinity, stronger currents and resulting decreasing plant cover on the fjord ground destroyed the opportunities of catching herring and freshwater fish (Andresen, 1856). Next to this channel, another flood opened the Thyborøn Channel in 1862. The new opening also silted up, but it was artificially opened again, so that the Limfjord today is a sound, connect-
7.3 Location

The Limfjord is a branched sound through northern Jutland, Denmark, connecting the North Sea with the Kattegat (Figure 7.2). The western and central Limfjord is characterised by large expanses of water with open bays, while the eastern part resembles a broad river (Andersen, 1990). The Limfjord today contains 7.4 km$^3$ water, has a surface area of 1500 km$^2$ and an average depth of 4.9 m. Sunlight reaches large parts of the Limfjord’s sea floor due to its shallowness (Andersen, 1995). From a drainage area of 7528 km$^2$, 2.7 km$^3$ fresh water enter the Limfjord per year. On average, there is a flow of 6.8 km$^3$ from the North Sea via Thyborøn Channel through the Limfjord to the Kattegat. Close to the eastward main current, the salinity varies with 2-4% from week to week (Grooss et al., 1996). It is about 30%, which compared to the North Sea’s 33% indicates a 10% dilution of the marine water with freshwater (Heier-Nielsen et al., 1995).

Kilen is a former fjord arm of the Limfjord (56° 30.005’N, 08° 34.089’E, Figure 7.2), located in a tunnel valley (Smed, 1981). It is surrounded by 25-35 m high slopes, has a mean water depth of 2.9 m and a surface area of 3.34 km$^2$ (Jensen et al., 2006). The catchment area of 35.3 km$^2$ includes two brooks, Bredkær bæk and Vasens bæk (Jensen et al., 2006).

Today, Kilen is a brackish embayment with salinity around 6‰, as sandspit formation and the construction of a dam in AD 1856 isolated Kilen from the main Limfjord (Ringkjøbing Amtskommune and Teknik- og Miljøforvaltningen, 1991). Beginnings of sandspit formation can be seen on historical maps, figure 7.3. Kilen is believed to have been naturally protected from strong currents, storms and wave action in the past, and hence a continuous sediment sequence has been preserved.

7.4 Methods

In 2010, five surface water samples were collected from different parts of the Limfjord (Figures 7.4, 7.5) for DIC water dating. Details on collection of water samples and CO$_2$-extraction can be found in chapter 3. In 2007, a ca. 1560 cm long sediment sequence was obtained from Kilen. The coring was made with a Russian peat sampler with a chamber length of 100 cm (Jowsey, 1966) in two parallel boreholes at a water depth of 390 cm below present sea level (bpsl). The sediments consist of homogenous grey-brown marine clay gyttja. Our analyses focus on the part between 467 and 1935 cm bpsl which was subsampled at 1-2 cm depth intervals. During the approximately 6100 years of our core, 1470 cm of sediments accumulated, so that the average sedimentation rate is 0.24 cm per year. The 1-2 cm depth intervals thus contain the record of ca. 4-8 years (depending on the actual sedimentation rate). Terrestrial plant macrofossils were radiocarbon dated and used to construct an age-to-depth model. Shells were dated to calculate reservoir ages. Stable isotope measurements (C,N) were performed on bulk organic matter samples from the sediment core. $\delta^{13}$C, $\delta^{15}$N, C/N ratio, carbon fraction and nitrogen fraction have been measured. Figure 7.1 illustrates the different samples for radiocarbon dating and stable isotope measurements.

Firstly, only 26 of the 60 samples were measured. The 26 largest samples were chosen, as it was not clear in the beginning how much material there had to be weighed out. After each measurement, the CO$_2$ and N$_2$ peak height indicated how much there had to be weighed out for the next measurement. Figure 7.6 shows the required weight for ideal $^{13}$C and $^{15}$N mea-
measurements, depending on the samples’ organic content as determined by LOI (see section 7.8). The functions fitted to the data points were used to estimate the sample size for the later weighing of the other 34 samples.

Chapter 3 gives details on sample collection, pretreatment, and radiocarbon and stable isotope measurements. $\delta^{13}$C and $\delta^{15}$N denote stable isotope measurements on bulk sediment organic matter, $\delta^{13}$C and $\delta^{18}$O measurements on foraminifera (see below) and shell carbonate are marked as $\delta^{13}$C$_{forams}$, $\delta^{18}$O$_{forams}$, $\delta^{13}$C$_{shell}$ and $\delta^{18}$O$_{shell}$, respectively.

Table 7.1 gives details on the pretreatment of the thirteen shell samples which I prepared in Aarhus. Four additional shell samples were later dated at the $^{14}$CHRONO Centre, Queen’s University Belfast, UK.

### 7.5 Chronology

The reservoir age $R$ of a shell sample can easily be calculated when a terrestrial sample from the same depth is available (see section 2.1.4 and Figure 7.8). Likewise, $\Delta R$ can be calculated as shown in Figure 7.8. However, when no terrestrial sample from the

Figure 7.2: Location of the Limfjord in Denmark, and Kilen in the Limfjord. Own work, made with MapInfo Professional 7.8 using bathymetry data by Thorkild Høy, published in Ringkjøbing Amtskommune and Teknik- og Miljøforvaltningen (1991).
same depth is available, the calibrated age $t$ of the shell is obtained from an age-to-depth model, whereafter $\Delta R$ can be calculated (Figure 7.9).

An age-to-depth model assigns an age to each cm of the core. Therefore, we also know the calendar ages of all the bulk sediment samples on which stable isotopes were measured.

The age-depth model is based on 13 $^{14}$C dated macrofossil samples of unequivocal terrestrial origin (Table 7.2). Six of these samples, the uppermost three and the lowermost three, were very small. All the carbon they yielded had to be used for $^{14}$C dating, and a $\delta^{13}$C measurement was not possible. For normalisation of the $^{14}$C dating, assumed $\delta^{13}$C values had thus to be used. An error of 1% in the $\delta^{13}$C measurement would in our case lead to an error of $8 \approx^{14}$C years, as we measured the $^{14}$C/$^{13}$C ratio. If the $^{14}$C/$^{13}$C ratio had been measured, e.g. in conventional dating, the error would have been 16 $^{14}$C years (see section 2.1.2 for detailed explanations and equations). At first, only two of the terrestrial macrofossils had been dated, AAR-11463 and AAR-11464. One of them, AAR-11463, contained enough carbon for a $\delta^{13}$C determination and resulted in $\delta^{13}$C=-28.36/permil. AAR-11464 was so small that a $\delta^{13}$C value had to be estimated. As only one extra sample from the same core was available for comparison, a standard value for terrestrial plants of -25/permil was assumed and used.
CHAPTER 7. THE LIMFJORD

Figure 7.4: Collection of surface water samples from the Limfjord

Figure 7.5: Reservoir ages of surface water samples from the Limfjord. The uncertainty of the reservoir age estimates is 20-22 years (all values can be found in table 7.3).
### Table 7.1: Shell samples from Kilen – Pretreatment

<table>
<thead>
<tr>
<th>SID</th>
<th>AAR</th>
<th>Sample weight [mg]</th>
<th>Weighed out for pretreatment</th>
<th>Amount of 1M HCl [μl]</th>
<th>Weight after pretreatment (yield [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>14253</td>
<td>13213</td>
<td>207.1</td>
<td>51.8</td>
<td>207</td>
<td>39.3 (75.9)</td>
</tr>
<tr>
<td>14254</td>
<td>13214</td>
<td>20.9</td>
<td>20.9</td>
<td>76</td>
<td>14.9 (71.2)</td>
</tr>
<tr>
<td>14255</td>
<td>13215</td>
<td>91.6</td>
<td>41.1</td>
<td>164</td>
<td>28.7 (69.8)</td>
</tr>
<tr>
<td>14256</td>
<td>13216</td>
<td>14.0</td>
<td>14.0</td>
<td>27</td>
<td>12.0 (85.7)</td>
</tr>
<tr>
<td>14257</td>
<td>13217</td>
<td>9.5</td>
<td>9.5</td>
<td>18</td>
<td>8.1 (85.3)</td>
</tr>
<tr>
<td>14258</td>
<td>13218</td>
<td>19.2</td>
<td>19.2</td>
<td>76</td>
<td>13.9 (72.4)</td>
</tr>
<tr>
<td>14259</td>
<td>13219</td>
<td>32.8</td>
<td>32.8</td>
<td>131</td>
<td>24.8 (75.6)</td>
</tr>
<tr>
<td>14260</td>
<td>13220</td>
<td>34.9</td>
<td>34.9</td>
<td>139</td>
<td>25.4 (72.8)</td>
</tr>
<tr>
<td>14261</td>
<td>13221</td>
<td>20.2</td>
<td>20.2</td>
<td>80</td>
<td>15.6 (76.7)</td>
</tr>
<tr>
<td>14262</td>
<td>13222</td>
<td>44.6</td>
<td>44.6</td>
<td>178</td>
<td>34.1 (76.5)</td>
</tr>
<tr>
<td>14263</td>
<td>13223</td>
<td>4.9</td>
<td>4.9</td>
<td>0</td>
<td>4.6 (93.9)</td>
</tr>
<tr>
<td>14264</td>
<td>13224</td>
<td>31.7</td>
<td>31.7</td>
<td>127</td>
<td>21.9 (69.1)</td>
</tr>
<tr>
<td>14265</td>
<td>13225</td>
<td>5.0</td>
<td>5.0</td>
<td>0</td>
<td>4.7 (94.0)</td>
</tr>
</tbody>
</table>

Figure 7.6: Required weight for isotope measurements, plotted versus organic content of sediment samples. Top, for δ¹³C measurements, bottom, for δ¹⁵N measurements.

#### 7.6 Results

The results from shell ¹⁴C dating and δ¹³C, δ¹⁸O measurements are presented in table 7.2 and figure...
7.11. Stable isotope measurements of bulk sediment are shown in figure 7.10. However, I begin with the water samples that were collected in the Limfjord in 2010.

### 7.6.1 Water samples

Surface water DIC collected in 2010 had $^{14}$C ages of -500 to -300 $^{14}$C years. For the calculation of reservoir age estimations, the pmC of the samples was compared to that of the contemporaneous atmosphere (Levin et al., 2010, and pers. comm. Ingeborg Levin 2012). This resulted in reservoir ages between -114 and +86 $^{14}$C years (Table 7.3 and Figure 7.5). Modern water samples collected in the Limfjord in 1996 yielded DIC reservoir ages between 110 and 450 $^{14}$C years, uncorrelated to sampling depth (pers. comm. Jan Heinemeier 2012). $\Delta R$ values of the modern water samples from 1996 and 2010 are thus in the range of -500 to +50 years. It is possible that bomb carbon, maybe some decades old and thus containing $>_{mod}$ern levels of $^{14}$C, entered the Limfjord and thus substantially reduced some of the reservoir effect measured today (cf. section 2.1.3). Modern surface water samples can thus only give very rough estimates of past reservoir ages and should not be used for correcting archaeological $^{14}$C datings.

### 7.6.2 Samples from the sediment core

#### Zone 1, 7300 cal BP-7000 cal BP

The shells from this zone yield $\Delta R$ values around 55 years. $\delta^{13}$C values are around -22 /permil and decrease to -24.6 /permil at ca. 7100 cal BP, the lowest value of the profile. This $\delta^{13}$C minimum is accompanied by a C/N ratio maximum of up to 18. $\delta^{15}$N values are between 3 and 3.5 /permil and increase to about 4 /permil at the top of the zone.

#### Zone 2, 7000 cal BP-5400 cal BP

This zone exhibits the largest variations in $\Delta R$. The shell with the highest $\Delta R$ of 300 years occurs in this zone at ca. 7100 cal BP. Two shells next to this one have $\Delta R$ values of -105 and -106 years, respectively. Two $\delta^{13}$C minima, approximately -23 and -24%, coincide with the two highest C/N values of the core, C/N > 18. In general, $\delta^{13}$C values are slightly increasing, and C/N ratios decreasing, especially at the top of this zone. In the lower half of the zone, $\delta^{15}$N values are relatively stable around 3%, but vary with
Table 7.2: Radiocarbon dates of shells and terrestrial macrofossils. If: leaf-fragment, lfs: leaf-fragments, bs: bud-scale, bss: bud-scales, t: twig, tf: twig-fragment. Scirpus seed: Scirpus maritimus/ lacustris. Numbers in squared brackets denote minimum salinity tolerances according to Sorgenfrei (1958). δ13C marked by an asterisk were measured by the accelerator and can only be used for normalisation of the 14C dating, not for drawing palaeoenvironmental conclusions. δ13C values in italics denote estimations for samples that were so small that all carbon had to be used for the 14C dating. See section 7.5 for discussion.

![Image](https://example.com/image.png)

Table 7.3: 14C dating of water samples from the Limfjord, collected by the crew of the Klitta (Figure 7.4. See figure 7.5 for a map of the sampling locations. For calculating the uncertainty of the reservoir age estimate, it was assumed that the measurement uncertainty of atmospheric pmC is negligible compared to measurement uncertainty of water DIC pmC.)

![Image](https://example.com/image.png)
ca. 1%/e in the upper half.

**Zone 3, 5400 cal BP-2000 cal BP**

ΔR decreases gradually from 70 to -55 yrs throughout this zone. The general trend towards less negative δ¹³C values continues to -20%/e. At the end of the zone, variation increases and δ¹³C and C/N ratio span ranges from -21.7 to -19.1%/e and from 11 to 15, respectively. δ¹⁵N values vary between 2.5 and 3.5%/e until they begin to increase after 4000 cal BP.

**Zone 4, 2000 cal BP-1300 cal BP**

ΔR ranges between -142 and 61 years. The highest δ¹³C-shell and lowest δ¹⁸O-shell of the profile occur at the bottom of this zone. δ¹³C values are around -21%/e and increase slightly. δ¹⁵N is highly variable in this interval. The maximum value for δ¹⁵N, 5.3%/e, occurs at 1700 cal BP. Following a C/N ratio peak of 16, the values remain quite stable around 13 and only increase to 14 at the top of the zone.
Figure 7.8: Calculation of the reservoir age \( R(t) \) and the local reservoir age offset \( \Delta R \) after radiocarbon dating of shell and terrestrial macrofossil from the same depth.
Figure 7.9: Calculation of the reservoir age \( R(t) \) and the local reservoir age offset \( \Delta R \) using the age-to-depth model when no terrestrial macrofossil from the same depth as the shell is available.
Figure 7.10: Measurements on bulk sediment organic matter: $\delta^{13}$C, C/N ratio and $\delta^{15}$N.
Figure 7.11: $^{14}$C datings and stable isotope values ($\delta^{13}$C, $\delta^{18}$O), of shell carbonate.
7.7 Discussion

7.7.1 $\delta^{13}$C, C/N, $\delta^{15}$N

Variations in $\delta^{13}$C and C/N values are commonly caused by changes in organic matter origin or primary organic productivity. In isolation basins, $\delta^{13}$C and C/N ratios have been used to distinguish marine and terrestrial organic matter (Mackie et al., 2007; Olsen et al., 2011). C/N ratios below 10 primarily reflect algae and C/N ratios above 20 terrestrial organic matter (Meyers and Teranes, 2001). Kilen C/N ratios range between 12 and 19 and span almost the entire range from algae to terrestrial organic matter (Figure 7.10). Marine organic matter has typically $\delta^{13}$C values between -16 and -22\%/permil (e.g. Mackie et al., 2007), freshwater organic matter between -35 and -25\%/permil and terrestrial organic matter between -30 and -25\%/permil (Meyers and Teranes, 2001). The $\delta^{13}$C values from Kilen range from -24.6 to -19.1\%/permil, i.e. between terrestrial and marine $\delta^{13}$C values. The low $\delta^{13}$C values (around -22\%/permil) and high C/N ratios (around 14) from the core base to ca. 5700 cal BP indicate that the organic matter content is dominated by a mixture of autochthonous and allochthonous sources. After 5700 cal BP, $\delta^{13}$C -22% and C/N <15 signify that autochthonous organic matter became increasingly important (Figure 7.10).

A strong correlation of the C/N ratios and $\delta^{13}$C values ($\rho$=-0.83, Figure 7.12) indicates a linear mixing between terrestrial and marine organic matter. Hence, both $\delta^{13}$C and C/N measurements distinguish marine from terrestrial organic matter. The correlation is strongest in zones 1 ($\rho$=-0.99) and 2 ($\rho$=-0.89). Productivity plays a minor role in determining the $\delta^{13}$C values in the Kilen sediments, although correlations between $\delta^{13}$C and TOC (indicating that productivity controls the $\delta^{13}$C values) can be observed for some periods, particularly in zone 4 ($\rho$=0.74, Figure 7.12). In conclusion, in periods with the strongest $\delta^{13}$C-TOC correlations, the $\delta^{13}$C-TOC correlation is very weak, and vice versa.

Major and rapid increases in C/N ratios associated with significant decreases in $\delta^{13}$C values around 7100 and 6000 cal BP (Figure 7.10) are probably caused by a large transfer of terrestrial organic matter into the sediments. These values may indicate transgression events, local increases of the relative sea level, in which large areas are inundated and terrestrial organic material is transported into the water. During the first centuries after each transgression event, $\delta^{13}$C values increase to values higher than before the transgressions. The higher sea level had possibly caused an increased distance from the shore to the coring location, thus limiting the input of terrestrial material, and increasing the relative importance of marine organic matter. Furthermore, nutrients released during the transgression can have enhanced marine productivity. Increasing autochthonous production also increases the relative importance of marine organic matter.

Total nitrogen and total organic carbon content, TN and TOC, are linearly correlated with an intercept of zero (Figure 7.13). Hence, only nitrogen of organic origin is present in our samples and we do not have to consider inorganic nitrogen, e.g. in the form of nitrates.

Organic matter nitrogen stable isotope values can be challenging to interpret because $\delta^{15}$N may depend on source organic matter, primary organic productivity and anaerobic processes of ammonification and denitrification (Talbot, 2001). Land plants have typical $\delta^{15}$N values of 2 to 10\%/permil, lake sediment -2 to 20\%/permil, and marine phytoplankton 3-12\%/permil (Talbot, 2001; Owens, 1987). The Kilen $\delta^{15}$N values between 2.5 and 5.3\%/permil fall within the normal range of marine and terrestrial $\delta^{15}$N values. The $\delta^{15}$N values are uncorrelated with $\delta^{13}$C and C/N ($\rho$=0.17 and -0.01 respectively) suggesting, contrary to $\delta^{13}$C, that $\delta^{15}$N cannot resolve the origin of the source organic matter. Ammonification and denitrification are also deemed unlikely to be able to explain the increasing $\delta^{15}$N values, due to the lack of supporting evidence from diatom, foraminifera and pigment analysis (Lewis, 2011; Lewis et al., submitted). The weak correlation between $\delta^{15}$N and TOC ($\rho$=0.51, Figure 7.12) suggests that the $\delta^{15}$N values are partly controlled by primary organic productivity (Figure 7.12). However, for zone 3, $\delta^{15}$N is stronger correlated with TOC ($\rho$=0.68). Combined with the generally low C/N values (average =13), i.e. autochthonous organic matter, this suggests a strong coupling with organic productivity. In most environments, nitrogen is a limiting nutrient for the production of organic matter. Therefore, an alternative explanation for the Kilen $\delta^{15}$N values is complete utilisation of dissolved inorganic nitrogen (DIN) during nitrogen assimilation by plankton and higher plants, leading to limited isotopic fractionation between organic matter and DIN (i.e. the organic matter $\delta^{15}$N will reflect $\delta^{15}$NDIN). Due to the close proximity of the core location to land, $\delta^{15}$N values likely reflect terrestrial $\delta^{15}$NDIN.

7.7.2 $\Delta R$ and $\delta^{13}$C, $\delta^{18}$O of shells

$\Delta R$ values range from -140 to 300 years (Figure 7.10, table 7.2). They are of the same order of magnitude as the values measured on 19th and 20th century (pre-
bombs) shells from the Limfjord (Heier-Nielsen et al., 1995). These measurements are in contrast to the radiocarbon dates of modern water samples which have ΔR values between -500 and +50 (see above).

In three cases, R_{direct} can be calculated directly by comparing the 14C ages of a shell sample and a terrestrial sample from the same depth. The differences between R_{direct} and R(t), calculated with the terrestrial age model, are 8±89, -80±191 and 57±107 14C-years. Thus within the large uncertainties the values agree.

There is no correlation between shell species and reservoir age, suggesting that species effects due to feeding habits or burrowing depths do not influence the reservoir age (cf. table 7.4). A similar conclusion was reached by studies of three other Danish fjords and the North Icelandic shelf (Olsen et al., 2009; Eiriksson et al., 2004).

Assuming a constant marine reservoir age of ca. 400 years (ΔR=0), it can be expected that the Kilen ΔR values are around 0 years during inferred marine conditions and more variable during brackish conditions.

The inferred relatively high-salinity bottom-water conditions, coinciding with brackish sea-surface conditions, during zone 1 display ΔR values around 55.
7.7. DISCUSSION

\[ y = 0.0878x - 7 \times 10^{-5} \]

\[ R^2 = 0.9804 \]

Figure 7.13: Total nitrogen and total organic carbon content of the Kilen sediment samples.

<table>
<thead>
<tr>
<th>AAR</th>
<th>Name</th>
<th>Species</th>
<th>Depth</th>
<th>Cal. Age BP</th>
<th>ΔR</th>
</tr>
</thead>
<tbody>
<tr>
<td>13213</td>
<td>R3C1</td>
<td><em>Tapes</em> <em>sp.</em></td>
<td>463-464</td>
<td>1212±27</td>
<td>101±34</td>
</tr>
<tr>
<td>13214</td>
<td>R3C1</td>
<td><em>Corbula gibba</em></td>
<td>473-474</td>
<td>1345±21</td>
<td>-131±34</td>
</tr>
<tr>
<td>13215</td>
<td>R3C3</td>
<td><em>Cerastoderma edule</em></td>
<td>525-526</td>
<td>1932±32</td>
<td>-129±33</td>
</tr>
<tr>
<td>13216</td>
<td>R4C2</td>
<td><em>Acta alba</em></td>
<td>598-600</td>
<td>2448±29</td>
<td>10±46</td>
</tr>
<tr>
<td>13217</td>
<td>R4C3</td>
<td><em>Cardium</em> <em>sp.</em></td>
<td>748-750</td>
<td>3433±12</td>
<td>7±39</td>
</tr>
<tr>
<td>13218</td>
<td>R4C6</td>
<td><em>Acta alba</em></td>
<td>972-974</td>
<td>4643±26</td>
<td>32±48</td>
</tr>
<tr>
<td>13219</td>
<td>R4C7</td>
<td><em>Corbula gibba</em></td>
<td>1146-1148</td>
<td>5318±16</td>
<td>90±43</td>
</tr>
<tr>
<td>13220</td>
<td>R4C8</td>
<td><em>Corbula gibba</em></td>
<td>1166-1168</td>
<td>5367±15</td>
<td>2±50</td>
</tr>
<tr>
<td>13221</td>
<td>R4C9</td>
<td><em>Acta alba</em></td>
<td>1276-1278</td>
<td>5623±11</td>
<td>-77±46</td>
</tr>
<tr>
<td>13222</td>
<td>R4C10</td>
<td><em>Acta alba</em></td>
<td>1400-1402</td>
<td>5965±11</td>
<td>35±39</td>
</tr>
<tr>
<td>13223</td>
<td>R4C11</td>
<td><em>Bittium reticulatum</em></td>
<td>1484-1486</td>
<td>6190±17</td>
<td>320±65</td>
</tr>
<tr>
<td>13224</td>
<td>R4C13</td>
<td><em>Corbula gibba</em></td>
<td>1708-1710</td>
<td>6871±31</td>
<td>-149±34</td>
</tr>
<tr>
<td>13225</td>
<td>R4C15</td>
<td><em>Tellina ferruginea</em></td>
<td>1924-1926</td>
<td>7330±24</td>
<td>34±150</td>
</tr>
</tbody>
</table>

Table 7.4: Shell samples from Kilen – Age of the layer in which the shell was found and ΔR. For each shell, some information about its habitat and/or feeding habits is given (from Rosenberg and Möller, 1979; Holmes and Miller, 2006; Fretter and Graham, 1981; Evagelopoulos et al., 2009; Bozilova and Beug, 1994; Barnes, 1994; sealifebase.org, 2009; marlin.ac.uk, 2009; conchsoc.org, 2009; marinespecies.org, 2009c,b,a; Petersen and Rasmussen, 1995). Numbers in squared brackets indicate salinity tolerances after Sorgenfrei (1958).
years. This may be a combined influence of normal marine water masses at the sea floor and an influence of 14C-free dissolved carbonates, i.e. hard water. During the inferred brackish conditions in zones 2 and 4, ΔR values are generally around -100, indicating a strong atmospheric/terrestrial influence. In zone 3, ΔR≈0 signifies marine conditions.

δ18Oshell ranges from -3.3 to -0.7‰, δ13Cshell from 0.4 to 2.9‰, corresponding to marine shell values of modern and historical samples (Keith et al., 1964; Burman and Schlüchter, 2005; Heier-Nielsen et al., 1995). Low δ13C and δ18O values of shell carbonate indicate a high terrestrial contribution/freshwater influence (see section 2.2 and e.g. Olsen et al., 2009): Decaying terrestrial plants release CO2 with low δ13C values, and δ18O values in precipitation are depleted relative to the ocean (Araguas-Araguas et al., 2000). When δ13Cshell and δ18Oshell are positively correlated, shell isotope values could thus be used to estimate the relative freshwater contribution (Mook, 1971). However, freshwater DIC can have high δ13C and δ18O values due to dissolved fossil carbonates being closer to ocean isotope values, because the carbonates originate from Cretaceous calcite (section 2.2.1). In the Kilen data, the correlation of δ13C and δ18O is negative (ρ=-0.69), and therefore shell carbonate isotope values cannot be used for palaeosalinity reconstruction. R(t) is not correlated with δ13Cshell or δ18Oshell, but one interesting event can be observed: The unusually high ΔR value around 6200 cal BP (zone 2) is supported by a relatively high δ13Cshell and probably influenced by 14C-free dissolved carbonates in hard freshwater. The high ΔR value is followed by a series of negative ΔR, when δ13Cshell values are also depleted (Figure 7.11), indicating terrestrial derived DIC, which has younger radiocarbon ages and lower δ13C values than ocean DIC.

Variability of δ18Oshell values can also be influenced by water temperature amounting to a change in δ18O of -0.24‰/°C (Craig, 1965). Higher δ18O values may correspond to lower temperatures and vice versa. However, due to the minor temperature variations during the Holocene (Brown et al., 2011), variations in salinity and oxygen source are expected to dominate the δ18Oshell isotope values. Intershell variability in δ18O can be over 4‰, as Burman and Schlüchter (2005) demonstrated on periwinkle shells from the Ertebølle locus classicus. These shells had negative summer δ18O values and positive winter values. All my shell samples have negative δ18O values, which would indicate that the majority of the shell carbonate was built up during summer. Burman and Schlüchter (2005) also observed a seasonality of δ13C values for Holocene shells, but not for recent gastropods.

7.8 Additional methods for the Kilen sediment core

Loss on ignition at 550°C and 925°C allowed estimation of organic matter (LOI) and CaCO3, respectively (Bengtsson and Enell, 1986; Dean, 1974), and was determined by Peter Rasmussen (GEUS). The total organic carbon content (TOC) was determined by the elemental analyser used for stable isotope measurements. TOC and LOI are equivalent measured for the proportion of organic matter in the sediment. As the sediment samples for stable isotope measurements were pre-treated with acid to remove carbonate, the carbon determined by the elemental analyser (chapter 3) originates exclusively from organic matter.

Mass accumulation rates (MAR, g/cm²/yr) of LOI, TOC and CaCO3 were calculated using the sediment dry density (g/cm³) and the accumulation rate (cm/yr) derived from the constructed age model. Other analyses on the same sediment sequence include diatoms, foraminifera, molluscs, terrestrial macrofossils and sedimentary pigments, and are described in detail in Lewis (2011); Lewis et al. (submitted).

A correlation of TOC and δ13C especially in zone 4, the zone with the largest TOC content (Figures 7.12 and 7.14), indicates that δ13C values are at least partly determined by productivity.

7.8.1 Results and Discussion

Selected results from the additional methods mentioned above will be presented here and put into context of the radiocarbon datings and stable isotope measurements. After a section about salinity in the photic zone and bulk sediment isotopes, the discussion is divided into the time intervals that were identified in the data, zones 1-4. The results of the geochemical analyses are presented in figure 7.14.
Figure 7.14: Sedimentary parameters: mass accumulation rates of CaCO₃, minerogenic and organic matter, measured as loss on ignition (LOI), and total organic carbon (TOC) measured with the EA. $\delta^{13}$C, C/N ratio, $\delta^{15}$N and $\Delta R$ are given for comparison.
Figure 7.15: Diatom-inferred (DI) salinity; added percentages of the marine (>25 psu) foraminifera Elphidium incertum, Elphidium magellanicum, Elphidium margaritaceum, Haynesina depressula, Bulimina marginata and Stainforthia sp. (Alve and Murray, 1999; Conradsen et al., 1994; Haake, 1962; Lutze, 1965, 1974; Murray, 1991); δ13C and δ18O values of shell carbonate and foraminifera Elphidium excavatum f. selseyensis; and, for comparison, sediment organic matter δ13C and local reservoir age ΔR.
\( \delta^{13}C \) and salinity in the photic zone

The photic zone is the uppermost layer of a body of water which is reached by enough light so that photosynthesis can take place. This is thus the zone of phytoplankton productivity. One important type of phytoplankton are diatoms, unicellular algae which have a cell wall, called frustule, of silica SiO\(_2\). Diatoms also include benthic/littoral forms, but common for all is that they require light for photosynthesis.

The salinity of the photic zone has been quantitatively reconstructed from diatom assemblages (Lewis et al., submitted; Lewis, 2011) and is shown in Figure 7.15. Interestingly, there is a strong correlation between the \( \delta^{13}C \) values and the diatom-inferred (DI)-salinity (\( \rho=0.69 \) excluding zone 4). High DI-salinities concur with high \( \delta^{13}C \) values, reflecting autochthonous marine organic matter. Low DI-salinities concur with low \( \delta^{13}C \) values and high C/N ratios, i.e. a higher proportion of terrestrial organic matter. This suggests that marine conditions enhance autochthonous organic productivity in contrast to freshwater/brackish conditions, during which the fraction of allochthonous organic matter is high.

Emeis et al. (2003) measured \( \delta^{13}C \) values of surface sediment and compared with modern salinity measurements. They found a linear correlation between the two variables, \( \delta^{13}C = -27.8 + 0.54 \times \text{salinity} \), \( R^2=0.85 \), for a salinity range of 1 to 12\%. A salinity range from -28.5 to -22.5\% is observed. If this equation was used for the Kilen sediment \( \delta^{13}C \) values, the reconstructed salinity (salinity = \( \delta^{13}C + 27.8 \)/0.54) would be between 5 and 16\% salinity. This is in contrast to the salinity reconstructed from diatom assemblages which indicates a minimum salinity of 19\% for the Kilen record. As almost all Kilen sediment \( \delta^{13}C \) values are outside the \( \delta^{13}C \) interval measured by Emeis et al. (2003), their model cannot be applied to our measurements. It would be interesting to expand the study of modern salinity and surface sediment \( \delta^{13}C \) values to higher salinities. If the linear relation continues to higher salinities, it will apparently not be applicable to sediment cores. However, it is also possible that the relationship is non-linear over larger ranges of salinity and \( \delta^{13}C \) values.

7.8.2 Zone 1, 7300 cal BP to 7000 cal BP (5350-5050 BC)

From the base of the core, \( \delta^{13}C \), C/N, diatoms and foraminifera indicate a highly productive environment with stratified, relatively deep water, brackish-marine salinity in the surface water and high salinity at the bottom (Figure 7.15 and Lewis et al., submitted). As we were able to retrieve about 15 m of sediment from a water depth of 4 m, we estimate that the water depth in Kilen was over 20 m during this zone (corrected for ca. 3 m of isostatic land rise). Stratification is a likely scenario because salinity differences of up to 6\% between surface and deep water still occurs in the Limfjord today (Grooss et al., 1996). The presence of a *Tellimya ferruginosa* suggests a bottom salinity of at least 30\% (Sorgenfrei, 1958), agreeing with a salinity of 31\% reconstructed from \( \delta^{13}C \) and \( \delta^{18}O \) values of periwinkles from the Ertebølle shell midden (eponymous site of the Ertebølle culture) in the central Limfjord (Burman and Schmitz, 2005).

Other studies agree with our environmental reconstructions (see also section 7.2 for other studies of the Limfjord). The highest level of the Littorina Sea in the south-western part of the Limfjord was about 2-3 m higher than today, and in the northern Limfjord, 5-6 m higher than today (chapter 5 and Mertz, 1924). The high sea level concurs with temperatures slightly higher than today, that resulted in an abundance of fish and the first occurrence of shell middens, consisting predominantly of oysters, in Denmark, the majority of which is from 6550-6350 cal BP (Brown et al., 2011; Enghoff et al., 2007; Andersen, 2007). Many settlements of the Ertebølle culture (ca. 7400-5000 cal BP) in the Limfjord region were inhabited for 1000-1500 years, and they were larger and closer to each other than in the rest of Denmark, most likely the consequence of a highly productive environment (Andersen, 1998). The dominance of oysters (80-90\%) in shell middens and natural shell banks between 7600 and 5700 cal BP indicates salinities of at least 23-25\% (Andersen, 2007; Jensen and Spärck, 1934; Yonge, 1960). Low \( \delta^{13}C \) values and high C/N ratios indicate a transgression around 7100 cal BP (Figure 7.10) which coincides with a minimum in sea surface DI-salinity and a maximum in bottom-water salinity as reflected in the foraminiferal record (Figure 7.15). Mineralisation of the terrestrial organic matter likely resulted in an increased nutrient supply which may be reflected in the increased \( \delta^{15}N \) values just after the transgression event and probably reflect increased productivity. Furthermore, the relatively high \( \Delta R \) values may reflect a terrestrial influence on DIC (Figure 7.11).

Transgression maxima or rising sea levels around 7100 cal BP were also demonstrated in the southern North Sea, on Sjælland, eastern Denmark and in the southern Baltic (Behre, 2007; Christensen, 1982; Hede, 2003; Christensen et al., 1997; Harff et al., 2005). However, when comparing sea-level curves, it must be kept in mind that transgression maxima generally occur later in south-western than in north-
eastern Denmark (Christensen, 1998; Hede, 2003).

### 7.8.3 Zone 2, 7000 cal BP to 5400 cal BP (5050-3450 BC)

In zone 2, δ¹³C and C/N signify a brackish marine environment (Figures 7.10, 7.12). From ca. 6900 to 5400 cal BP, foraminifera and diatoms suggest periodic stratification of the water column. The concentration of high-salinity (>25%) demanding foraminifera at the bottom is high, but variable, while diatoms indicate brackish-marine surface waters with salinities occasionally down to 20% (Figure 7.15). δ¹⁸O and δ¹³C values of foraminifera (Elphidium excavatum f. selsegensis) are available from about 6600 cal BP (4650 BC) and are proxies for bottom water salinity. High δ¹⁸O_forams values in 6600-4650 cal BP, and thus high bottom salinity, agree with the inferred stratification of the water column. The bottom water is freshening gradually until 4650 cal BP. δ¹³C_forams are negative which indicates greater utilisation of terrestrial derived CO₂ under stratified conditions (Lewis et al., submitted). Another transgression event at ca. 6000 cal BP (δ¹³C minimum, C/N maximum) is associated with decreased ΔR, δ¹³C_shell and DI-salinity as well as increasing plant macrofossil concentration (Lewis et al., submitted) supporting increased terrestrial influence on DIC (Figures 7.10, 7.15). In other regions of Denmark and the Baltic, transgression maxima or rising sea levels can be found at this time, though less pronounced than at 7100 cal BP (Christensen, 1982; Harff et al., 2005; Christensen et al., 1997). We can thus identify two transgressions during the Atlantic period (ca. 7800-5700 cal BP, see section 5.1). Other studies have found three or four episodes of high sea level in Denmark during the Atlantic (cf. Christensen, 1995). However, at Halsskov Fjord on the west coast of Sjælland, sea level curves agree with our data and only show two Atlantic transgressions (Christensen et al., 1997).

After ca. 6000 cal BP, foraminifera and diatoms indicate some salinity fluctuations (Figure 7.15). Furthermore, numerous Bittium reticulatum and occasional T. ferruginosa suggest frequently relatively high salinity (Lewis, 2011).

At the time of the mid-Holocene elm decline, around 5900 cal BP, plant macrofossil and sedimentary pigment analyses indicate a reduction in forest density and increased inputs of terrestrial organic matter, which most likely is associated with anthropogenic catchment disturbances (Lewis, 2011). An increased number of Betula fruits in the plant macrofossil record after 5800 cal BP likely reflects the early Neolithic Betula expansion which can be identified in pollen diagrams (Iversen, 1941). Betula is a light-demanding tree and profits from anthropogenic forest clearances. At Kilen, the first evidence of agriculture is witnessed by the appearance of ribwort plantain pollen (Plantago lanceolata, Iversen, 1941). The first P. lanceolata pollen are from 5850 cal BP and a continuous curve begins around 5600 cal BP (Lewis, 2011; Lewis et al., submitted). In the western Limfjord region, P. lanceolata pollen occur at 5750 cal BP (Andersen, 1992-93). However, the minerogenic flux - a proxy for catchment soil erosion - does not increase substantially until after 5400 cal BP.

Elevated δ¹³C and decreasing C/N show increased marine influence after 5600 cal BP. This may be associated with a strengthening of the Jutland current and increased inflow of North Sea water into the Kattegat (Gyllencreutz and Kissel, 2006; Conradsen and Heier-Nielsen, 1995). The Jutland current erodes and re-deposits sediments along the western and northern coast of Jutland, and may therefore have impacted the opening or closing of connections between the Limfjord and the North Sea or Skagerrak.

### 7.8.4 Zone 3, 5400 cal BP to 2000 cal BP (3450-50 BC)

From 5400 cal BP, the minerogenic content increases strongly until 4600 cal BP suggesting increased catchment erosion (Figure 7.10) which concurs with the “landnam” phase (Iversen, 1941), a period of forest clearances and the first traces of major agricultural activities starting around 5500 cal BP (Andersen, 1992-93). This is supported by pollen analyses from Thy, north-west of the Limfjord, where a sudden and large-scale clearance period is indicated in 4750-3750 cal BP (2800-1800 BC) by pollen of herbs, but also cereals (Andersen, 1992-93). After 4600 cal BP, the minerogenic content is roughly constant and remains high (Figure 7.10) suggesting a more constant human influence. Foraminifera and diatoms indicate approximately similar salinity conditions in surface and bottom waters, suggesting a well-mixed water column (Lewis et al., submitted). Bottom water salinity as derived from δ¹⁸O_forams apparently increases after 4650 cal BP. This is interpreted as a decreasing degree of water column stratification, and δ¹⁸O_forams begins to reflect overall water column salinity (Lewis et al., submitted). Isostatic uplift, in combination with the lower rate of the eustatic sea level rise reduced the depth of Kilen. It may have contributed to the transition from strong water column stratification to a well mixed water column. The increased δ¹³C and low C/N ratios of the sediment, and relatively high DI-salinities, show an increased marine influence, prob-
ably caused by greater exposure to the North Sea in the western Limfjord. A $\delta^{13}C_{\text{forams}}$ increase of 0.5-1% supports the interpretation of greater mixing with open marine water (Lewis et al., submitted). This is coincident with a transgression in the Limfjord from around 4800-4240 cal BP (Petersen, 1976) and a sea-level highstand around 4700 cal BP at Skagen, northern Jutland (Clemmensen et al., 2001b). The foraminiferal assemblages indicate unstable environmental conditions from 3650 cal BP, and the stronger wave action and shallower water are likely to have contributed to a weakening of the water column stratification. Between 4000 and 3500 cal BP, high $\delta^{13}C$ values and very low C/N ratios indicate a high fraction of marine organic matter and thus high autochthonous productivity. Archaeological finds and $\delta^{13}C$ values of human bones from the Limfjord region still indicate the importance of fishing and shell collection (Andersen, 2007). This agrees well with the almost fully marine conditions inferred from the $\delta^{13}C$ values and C/N ratios. In zone 3, $\delta^{15}N$ and TOC are correlated ($\rho = 0.68$), suggesting that the $\delta^{15}N$ values are governed by primary organic productivity or $\delta^{15}N$ enriched DIN from the catchment. The $\delta^{15}N$ values of crops can increase by up to 3.5% due to manuring (Fraser et al., 2011). Interestingly, increasing $\delta^{15}N$ values from ca. 3500 cal BP concur with a shift of focus in agricultural practice from farming to cattle husbandry in the western Limfjord region (pers. comm. S. H. Andersen). An increase in the number of cattle around Kilen would have had a manuring effect on the pasture and increased the $\delta^{15}N$ values of the DIN in the Kilen catchment. The change in agriculture may have been provoked by climate: Several studies show a climate deterioration with lower temperatures in southern Scandinavia after ca. 4500 cal BP (Brown et al., 2011), increased storminess at ca. 4200 cal BP both in north- and south-western Jutland (Clemmensen et al., 2006, 2001a) and increased precipitation in Denmark during the last 3700-4300 years (Olsen et al., 2010b). Cereal yields may have decreased due to this climate deterioration. Hence we speculate that the change in cultural practice could be induced by climate change making cattle the better option, particularly on the relatively poor soils around Kilen. This is supported by pollen diagrams from the western Limfjord area which indicate an expansion of pasture at the same time (Andersen, 1992-93).

Between 2800 and ca. 2000 cal BP, the $\delta^{13}C$ values and C/N ratios suggest marine but unstable conditions with variable input of terrestrial organic matter, perhaps due to variable amounts of freshwater inflow (Figure 7.10). A possible freshwater event is also recorded in the $\delta^{18}O_{\text{forams}}$ values (Figure 7.15 Lewis et al., submitted). A strong marine influence is supported by the increasing DI-salinity (Figure 7.15) which is consistent with micro- and macrofauna records from Bjørnsholm Bay (Christensen et al., 2004; Kristensen et al., 1995) and continuous marine sedimentation until ca. 2200 cal BP at Agger Tange (Petersen, 1985a). Around 2400 cal BP, a high relative sea level persisted in the Skagen region (Clemmensen et al., 2001b) and a marine transgression phase began in the southern North Sea (Behre, 2007). In the Pre-Roman Iron Age (2450-1950 cal BP), the archaeological record in the Limfjord area includes fishbones and molluscs (mussels, cockles and oysters) indicating that marine resources were important (Andersen, 1998), in concord with the inferred marine conditions (Figures 7.10, 7.15). $\Delta R$ values zero also reflect marine conditions. Only at the boundary between zones 2 and 3, the $\Delta R$ values are slightly higher, around 100 years (Figure 7.10).

### 7.8.5 Zone 4, 2000 cal BP to 1300 cal BP (50 BC-AD 650)

Around 2000 cal BP (50 BC), a dramatic environmental change is recorded in the Kilen sediments. Low DI-salinity and the disappearance of marine foraminifera indicate brackish conditions, whereas maxima in organic matter and minerogenic MAR are recorded at ca. 2000 cal BP (Figures 7.10, 7.15). The increased accumulation of minerogenic material might have isolated Kilen from the Limfjord, and/or the isolation hindered the removal of minerogenic material from Kilen, which lead to an increased MAR. Negative $\Delta R$ values at 1900 and 1700 cal BP can be caused by a reduced connection of Kilen with the Limfjord, resulting in a larger extent in equilibrium of its water with the atmosphere, which is in agreement with the low salinity and the general decrease in water depth. The indication of a shift from open marine to brackish conditions by the $\delta^{13}C$ and C/N values is supported by evidence at Bjørnsholm Bay (Christensen et al., 2004; Kristensen et al., 1995). Therefore, this shift in the marine environment appears to include the whole Limfjord which most likely was cut off from the North Sea and Skagerrak at that time. The organic productivity in Kilen increases substantially after 2000 cal BP, as indicated by increasing organic matter MAR and supported by a maximum in CaCO$_3$ MAR (Figure 7.10), probably caused by carbonate precipitation due to increased photosynthetic activity removing CO$_2$ from the water. The archaeological record in the Limfjord region and $\delta^{13}C$ measurements on human bones from ca. 1550 to 900
cal BP show a reduced utilisation of marine resources (Andersen, 1998). It is unclear whether this change is caused by the less marine conditions observed for the Limfjord, or whether the change in human diet preferences has a cultural background. The period around 1500 cal BP, with high δ13C values, concurs with low C/N ratios indicating autochthonous organic matter. Between 1360 and 1200 cal BP, there is a short-term re-appearance of marine (>25%) foraminifera (Figure 7.15). At 1250 cal BP, ΔR indicates a marine reservoir age (Figure 7.10). Hence, both foraminifera and ΔR suggest that the isolation of Kilen was only of short duration.

7.9 Conclusion

In the sediment record from Kilen in the Limfjord, northern Denmark, δ13C values and C/N ratios of sediment organic matter are strongly correlated and reflect source organic matter. A linear mixing of marine and terrestrial matter can be observed. δ13C values also correlate with a diatom-inferred (DI) quantitative reconstruction of salinity and can thus be used as a proxy for salinity estimation in the photic zone. During freshwater/brackish conditions, the sediment organic matter is dominated by terrestrial input, whereas marine conditions enhance autochthonous production.

In the interval 7300-7000 cal BP (zone 1), the water is relatively deep and salinity-stratified with brackish sea-surface conditions and high-salinity bottom waters. A transgression event occurred around 7100 cal BP with minima in δ13C and DI-salinity and a maximum in bottom water salinity. A subsequent δ15N maximum reflects increased organic productivity caused by mineralisation of terrestrial organic matter that had entered Kilen during the transgression. ΔR values around +55 years may be influenced by mixing of high-salinity bottom waters and 14C-depleted freshwater with a hardwater effect, further supporting the interpretation of relatively brackish surface waters. The high bottom water salinity indicates an unimpeded connection between the Limfjord and the open ocean. However, as many proxies indicate a low-energy environment, the connection(s) to the ocean must have been at some distance from Kilen, and we suggest that the northern Limfjord was substantially exposed to the Skagerrak during this time interval.

In the interval 7000-5400 cal BP (zone 2), δ13C, C/N and DI-salinity indicate another transgression at around 6000 cal BP. This zone is characterized by negative ΔR values that presumably are caused by a freshwater influence with terrestrial derived DIC. A ΔR value around 300 years at ca. 6300 cal BP can only be a result of the hardwater effect, implying a large contribution of carbonate-rich freshwater. TOC and TN increase through zone 2 and reach stable values in the interval 5400-2000 cal BP (zone 3). Zone 3 is furthermore characterised by increasingly more marine conditions, as shown by increasing δ13C and DI-salinity, decreasing C/N and ΔR around zero. Surface salinity increases, while bottom salinity decreases, indicating that the previously stratified water column now became mixed.

The interval 2000-1300 cal BP (zone 4) represents a highly productive brackish environment with relatively low water depth and varying ΔR, which alternately shows an increased exchange with the atmosphere (negative ΔR) and a small influence from the hardwater effect (positive ΔR). The DI-salinity reaches a minimum of about 15%, but is no longer correlated with δ13C. The δ13C values and C/N ratios only show a limited terrestrial influence and are dominated by autochthonous production, which is in agreement with indications of high productivity such as high CaCO3 MAR, TN, TOC and δ15N. We suggest that the salinity changes observed in zones 3 and 4 show increased marine influence in the western part of the Limfjord (through the western opening of the fjord towards the North Sea), whereas the northern openings diminished as a result of isostatic uplift, aeolian sand transport and redeposition of sediment by ocean currents, mainly the Jutland current. Additionally, reduced connection of Kilen to the Limfjord should be considered.

Generally, δ15N values do not follow the development in the brackish/marine environment. The values appear to reflect changes in the catchment of Kilen and vary only slightly until a major increase after ca. 3500 cal BP, which may reflect a change in agriculture as a response to a cooler climate. In general, the Kilen record shows a gradual increase in anthropogenic influence, from the first catchment disturbances beginning around the time of the elm decline (ca. 5900 cal BP) over the first substantial traces of agriculture (ca. 5600 cal BP) and intensification of agriculture (5400–4600 cal BP) to possibly heavier dependence on cattle after 3500 cal BP.

As the reservoir ages are variable in zones 1, 2, and 4, no single value for a reservoir correction can be obtained. The absolute values and degree of variability, however, is much smaller than in freshwater rivers (cf. chapter 6). From 5000 to 2000 cal BP, however, a marine reservoir age of ΔR=0 can be applied to samples from the Limfjord.

In conclusion, the good agreement of the different
proxies with each other and with previous studies shows the strength of the different methods. Various aspects of the palaeoenvironment have been ascertained and indicate the development of Kilen and the Limfjord. As a result of the shore-near location of the core, some processes on land have furthermore been reflected in the sediment record. A multi-proxy approach like the present study is thus a powerful tool for the reconstruction of the aquatic and terrestrial environment and for the detection of anthropogenic changes.
Chapter 8

Conclusions and Summary

In this chapter, I will shortly summarize the main results from chapter 4, 6 and 7.

8.1 Method Development

Food crusts on pottery, but also shells and terrestrial macrofossils from a sediment core, are often very small samples. I have therefore investigated some possibilities for improving the preparation of these small sample for radiocarbon dating.

It is possible to combine CO$_2$ collection during stable isotope measurements with trapping of the CO$_2$ to measure its amount without changing the isotope ratios or radiocarbon ages of the trapped gas. However, the trapped yield is too low and too variable. A carefully designed trap could increase the yield, and especially a zeolite trap should be considered.

CO$_2$ collection from the elemental analyser would avoid fractionation and contamination introduced by quartz tube combustion of small samples.

For the graphitisation of small samples, the reactor volume should be reduced in order to secure effective graphitisation and minimize fractionation. Furthermore, the use of iron instead of cobalt as catalyst is recommended.

When a new accelerator is installed at the AMS $^{14}$C Dating Centre in Aarhus, the method development will be continued to optimize the performance of small samples in the new ion source and accelerator.

8.2 Freshwater reservoir effect variability

The freshwater reservoir effect was measured on different materials from Northern German rivers. The aim was to understand the mechanisms behind it, and to quantify its order of magnitude and degree of variability in order to predict the possible error in radiocarbon dating of Stone Age samples originating from these rivers.

As a result, freshwater reservoir effects in rivers are large and highly variable. The DIC $^{14}$C age, for example, depends on the amounts of precipitation in the week before sampling. Radiocarbon ages of over 2000 years could be measured on water DIC and aquatic plants, in spite of the effect of bomb carbon. Apparently, the reservoir age of aquatic plants or animals does not depend on the species. Floating leaves, for example, can have higher radiocarbon ages than submerged plants. Age differences as high as 1500 14C years are possible for plants collected on the same day in the same part of the river. It is therefore not possible to assign a precise reservoir age to a river.

Radiocarbon might in future studies be used to identify the carbon source of aquatic plants, and to map food webs in freshwater systems.

8.3 Radiocarbon dating of pottery

Radiocarbon dating of pottery from inland sites in Northern Germany had resulted in sensationally high ages. Therefore, the possibility of a freshwater reservoir effect was examined. As mentioned above, reservoir effects in the regions are potentially very high.

Experiments, during which food crusts were produced from different aquatic and terrestrial ingredients, proved that the reservoir age of the ingredients is reflected in the reservoir age of the food crust on pottery. The freshwater reservoir effect must therefore be considered when dating pottery from inland sites, and the sensationally old pottery is in all likelihood not older as similar pottery from coastal settlements.

$\delta^{13}$C and $\delta^{15}$N values cannot be used to precisely reconstruct palaeocuisine, i.e. the complete recipe which was cooked in the pot. However, they can indicate the risk of a freshwater or marine reservoir effect,
and identify the ingredients that scorched on the part of the sherd which is analysed.

For \( \delta^{13}C \) and \( \delta^{15}N \) measurements, food crusts on pottery do not need to be chemically pre-treated. For radiocarbon dating, food crusts can be pre-treated by the AAA method, which is also used for charcoal. Furthermore, protein extraction by a simple modified Longin method can be applied to food crusts on pottery. However, this requires large samples, >500 mg, and an optimised method for taking the food crust protein out of the pre-treatment vials.

Lipid analysis of food crusts is feasible and many of the modern food crusts were identified correctly. However, lipids in archaeological pottery seem to be less well preserved than lipids in the ceramic matrix. Radiocarbon dating of lipids extracted from ceramic sherds or food crusts is possible, although some of the ages appear too young or too old. Some of the oldest lipid dates were made on remains that were classified as “dairy”. As dairying at such early times is improbable, the radiocarbon date or the lipid analysis may be inaccurate. The only material that with absolute certainty is associated with the lipids are food crusts on the same sherds. As these can be affected by a reservoir effect, the true age of the pottery can be difficult to determine. Future studies will focus on understanding the mechanisms that lead to inaccurate lipid dates. Sample extraction and collection should be systematized, and the radiocarbon dating of single fatty acids will be attempted. With this strategy, marine and terrestrial lipids from the same sherd could be dated individually, and precise reservoir ages as well as accurate pottery dates would be obtained.

Ideally, pottery from different cultures from all over Northern Europe will be dated with the same method to obtain comparable results. Reservoir effects should be identified and corrected. Then it would be possible to follow the spread of the earliest pottery throughout Northern Europe in detail.

FTIR spectroscopy has some potential for characterizing food crusts, but is very complicated. More work needs to be done before FTIR spectroscopy can be used as a routine screening method for radiocarbon dating or other analyses of food crusts on pottery. However, the basis for a reference library is provided with the spectra recorded during this study. Petrographic microscopy, in contrast, cannot add new information to the analysis of food crust samples.

### 8.4 The Limfjord

Since its formation after the end of the last glaciation, the Limfjord has been an attractive environment for human habitation. People have adapted to the various resources the Limfjord provided, but have increasingly shaped the environment, from the first forest clearances in the beginning of the Neolithic to the artificially maintained opening of the Limfjord to the North Sea today. For understanding the mutual interaction between people and their environment, accurate datings of cultural phenomena and environmental records are essential. In an estuarine system like the Limfjord, radiocarbon dating is complicated because of the combination of marine and freshwater reservoir effects. The chapter on the Limfjord focused therefore on the long-term variability of the reservoir age, in combination with the reconstruction of natural and anthropogenic environmental changes during the mid- to late Holocene.

Radiocarbon reservoir ages and stable isotope ratios of bulk sediment organic matter agree well with environmental reconstructions from other proxies. The reservoir age in this part of the Limfjord is much lower and less variable than in the Northern German rivers. Reservoir ages were measured on shells which had developed throughout the life time of the mollusks. Therefore, shells represent the mean radiocarbon age of several years and average over short-term fluctuations.

\( \delta^{13}C \) values and C/N ratios of bulk sediment organic matter are strongly correlated with each other and with the salinity in the photic zone, as reconstructed from diatom assemblages. This indicates that autochthonous productivity is high in the marine environment, while sediments from brackish phases are dominated by allochthonous terrestrial organic matter. \( \delta^{15}N \) values of sediment organic matter reflect changes in the catchment and depend to a lesser degree on processes in the aquatic environment.

Kilen, the fjord arm analysed in this study, is relatively deep and salinity-stratified around 7000 cal BP (5000 BC). The high bottom salinity indicates a strong connection of the Limfjord to the North Sea or Skagerrak. At the same time, low wave energies are indicated for Kilen. The connection of the Limfjord to the ocean was thus probably in the north, and not in the west as the present-day connection. The depth of Kilen decreases during the subsequent millennia as a result of sedimentation and isostatic land rise. Bottom water salinity decreases while surface water salinity increases. Two transgression events in 7100 and 6000 cal BP were identified. In 2000 cal BP, a change towards a brackish, high-productivity environment can be observed.

In the interval 5000–2000 cal BP (3040–50 BC), the mollusks from Kilen have marine reservoir ages. In 7300–5000 cal BP and after 2000 cal BP, reser-
voir ages are more variable. Values between $R = 700$ and 250 $^{14}$C years indicate alternating hardwater influence and terrestrial organic carbon or enhanced atmospheric exchange. In this part of the Limfjord, radiocarbon dates on organisms originating from the fjord, including bones of humans that depended on marine resources, can be corrected with a reservoir age of 400 years for the period 5000–2000 cal BP (3040–50 BC). However, samples older than 5000 cal BP or younger than 2000 cal BP can be affected by a reservoir effect which is much more difficult to quantify, and reservoir ages of up to 700 years must be considered.

8.5 Summary

Further improvement of the preparation of small samples for radiocarbon dating will greatly improve future studies on cultural or environmental developments. It will be possible to date small samples from pottery, such as plant inclusions or food crusts, but also small samples from sediment cores, so that terrestrial age models can be constructed for environments with small amounts of terrestrial macrofossils.

Large and highly variable freshwater reservoir ages are a source of considerable errors in radiocarbon dating of different samples from inland contexts. They also influence the reservoir effect of estuarine environments, albeit variations in these contexts tend to be reduced.

Freshwater systems cannot be characterized by a constant reservoir offset, and the correction of radiocarbon dates is thus complicated. However, the reservoir reservoir effect can also be a source of information. The origin of water masses in an estuarine system, i.e. the relative proportions of marine and freshwater, can be estimated. Furthermore, the freshwater reservoir effect may help to identify carbon pathways in aquatic systems.

When pottery from inland sites is dated by radiocarbon dating of food crusts, a freshwater reservoir effect must be considered. It can introduce large age deviations and may not always be reflected in the stable isotope ratios of the food crusts. However, accurate and precise radiocarbon dating is essential for understanding the complex history of the introduction of pottery in Northern Europe. Therefore, reservoir effects must be attempted to be quantified, or at least identified.
Appendix A

Graphitisation test samples for radiocarbon dating

The following table summarises the graphitised samples from chapter 4, for which pressure curves had been recorded. Samples above 1mgC are only listed in this table if their graphitisation and mounting differed from the standard method. The pmC of standard materials is given in table 4.5 in chapter 4. Some samples were mounted in pre-drilled cathodes by hammering, in contrast to the usual pressing (cf. section 2.1.2). Samples which could not be measured are marked with —.

<table>
<thead>
<tr>
<th>Material</th>
<th>C-no.</th>
<th>mgC</th>
<th>reactor, catalyst</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>bgd gw</td>
<td>20048</td>
<td>0.013</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd gw</td>
<td>20049</td>
<td>0.013</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
<td>SID 12347 arch. sample</td>
<td>20502</td>
<td>0.027</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
<td>SID 12393 arch. sample</td>
<td>20503</td>
<td>0.028</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd wood</td>
<td>20078</td>
<td>0.093</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
<td>SID 12344 arch. sample</td>
<td>20495</td>
<td>0.093</td>
<td>R, Fe</td>
<td>terminated; no output in ion source</td>
</tr>
<tr>
<td>bgd wood</td>
<td>20079</td>
<td>0.120</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
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<td>20513</td>
<td>0.130</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
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<td>20512</td>
<td>0.133</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>20206</td>
<td>0.133</td>
<td>r, Co</td>
<td>small cathode, hammered, pmC 103.48±1.49</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>20236</td>
<td>0.120</td>
<td>r, Co</td>
<td>pmC 1.07±0.06</td>
</tr>
<tr>
<td>bgd wood</td>
<td>20238</td>
<td>0.130</td>
<td>r, Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>20239</td>
<td>0.133</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>20235</td>
<td>0.133</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>20229</td>
<td>0.150</td>
<td>r, Co</td>
<td>small cathode, hammered, pmC 0.90±0.05</td>
</tr>
<tr>
<td>Ox-I</td>
<td>20207</td>
<td>0.173</td>
<td>r, Co</td>
<td>pmC 103.91±1.06</td>
</tr>
<tr>
<td>bgd wood</td>
<td>0.19</td>
<td>24480</td>
<td>r, &lt; 2 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd wood</td>
<td>0.19</td>
<td>24481</td>
<td>r, 0.34 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21199</td>
<td>0.200</td>
<td>r, Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>0.20</td>
<td>24470</td>
<td>r, 0.39 mg Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>0.20</td>
<td>24471</td>
<td>r, 1.38 mg Co</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>0.21</td>
<td>24466</td>
<td>R, 0.80 mg Co</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21198</td>
<td>0.210</td>
<td>r, Co</td>
<td>pmC 103.95±0.39</td>
</tr>
<tr>
<td>bgd gw</td>
<td>20046</td>
<td>0.235</td>
<td>R, Fe</td>
<td>pmC 1.24±0.44</td>
</tr>
<tr>
<td>Gel A</td>
<td>0.24</td>
<td>24316</td>
<td>r, Co</td>
<td>pmC 107.31±0.52</td>
</tr>
<tr>
<td>Gel A</td>
<td>0.25</td>
<td>24315</td>
<td>r, Co</td>
<td>pmC 107.39±0.55</td>
</tr>
</tbody>
</table>
## APPENDIX A. GRAPHITISATION TEST SAMPLES FOR $^{14}C$ DATING

<table>
<thead>
<tr>
<th>Material</th>
<th>C-no.</th>
<th>mgC</th>
<th>reactor, catalyst</th>
<th>status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel A</td>
<td>20498</td>
<td>0.280</td>
<td>R, Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>20236</td>
<td>0.280</td>
<td>R, Fe</td>
<td>pmC 1.07±0.06</td>
</tr>
<tr>
<td>arch. sample from another user</td>
<td>20224</td>
<td>0.320</td>
<td>R, Co</td>
<td>pmC 76.4±0.21</td>
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<tr>
<td>bone collagen SID 12608</td>
<td>20497</td>
<td>0.370</td>
<td>R, Fe</td>
<td>pmC 38.73±0.50 (residue after collagen extraction: normal size cathode, extern graphitisation, pmC 39.93±0.16)</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>20510</td>
<td>0.460</td>
<td>R, Fe</td>
<td>pmC 50.58±0.05</td>
</tr>
<tr>
<td>bone collagen SID 12342</td>
<td>20494</td>
<td>0.470</td>
<td>R, Fe</td>
<td>pmC 45.24±0.36 (a sample from the same bone: C-20125, 0.89mgC, pmC 45.79±0.37)</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>20511</td>
<td>0.470</td>
<td>R, Fe</td>
<td>pmC 50.58±0.05</td>
</tr>
<tr>
<td>bone collagen SID 12066</td>
<td>20496</td>
<td>0.65</td>
<td>R, Fe</td>
<td>pmC 38.64±0.32 (residue after collagen extraction: extern graphitisation, 0.574mgC, pmC 33.81±0.16)</td>
</tr>
<tr>
<td>Gel A</td>
<td>24477</td>
<td>0.93</td>
<td>R, 2.0 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>Gel A</td>
<td>24476</td>
<td>0.95</td>
<td>R, 0.83 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>24465</td>
<td>0.97</td>
<td>R, 0.49 mg Co</td>
<td>pmC 0.83±0.03</td>
</tr>
<tr>
<td>bgd wood</td>
<td>24472</td>
<td>0.97</td>
<td>R, 2.53 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd wood</td>
<td>24474</td>
<td>0.97</td>
<td>R, 0.67 mg Fe + 1.58 mg Cr</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21197</td>
<td>0.980</td>
<td>R, Co</td>
<td>pmC 105.75±0.18</td>
</tr>
<tr>
<td>Gel A</td>
<td>24478</td>
<td>0.98</td>
<td>R, 0.52 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>Gel A</td>
<td>24479</td>
<td>0.99</td>
<td>R, 0.19 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21090</td>
<td>0.998</td>
<td>R, Co</td>
<td>cathode hammered Ø 1mm, depth 2mm, no pressure curve, pmC 103.46±0.95</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>24467</td>
<td>1.00</td>
<td>R, 2.64 mg Co</td>
<td>pmC 0.58±0.02</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>24468</td>
<td>1.00</td>
<td>R, 1.43 mg Co</td>
<td>pmC 0.54±0.02</td>
</tr>
<tr>
<td>bgd db sp</td>
<td>24469</td>
<td>1.00</td>
<td>R, 0.66 mg Co + 0.90 mg Cr</td>
<td>pmC 0.55±0.02</td>
</tr>
<tr>
<td>Ox-I</td>
<td>20509</td>
<td>1.01</td>
<td>R, Fe</td>
<td>pmC 103.02±0.40</td>
</tr>
<tr>
<td>bgd wood</td>
<td>24473</td>
<td>1.01</td>
<td>R, 0.55 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21092</td>
<td>1.013</td>
<td>R, Fe</td>
<td>—</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21093</td>
<td>1.019</td>
<td>R, Fe</td>
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<tr>
<td>bgd db sp</td>
<td>24464</td>
<td>1.04</td>
<td>R, 0.21 mg Co</td>
<td>pmC 0.70±0.03</td>
</tr>
<tr>
<td>Ox-I</td>
<td>21086</td>
<td>1.054</td>
<td>R, Co</td>
<td>hammered Ø 1mm, pmC 103.02±0.40</td>
</tr>
<tr>
<td>bgd wood</td>
<td>24475</td>
<td>1.06</td>
<td>R, 0.84 mg Fe</td>
<td>—</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>20501</td>
<td>1.06</td>
<td>R, Fe</td>
<td>pmC 0.34±0.02</td>
</tr>
<tr>
<td>bgd anthracite</td>
<td>20500</td>
<td>1.09</td>
<td>R, Fe</td>
<td>pmC 0.27±0.01</td>
</tr>
<tr>
<td>Ox-I</td>
<td>20508</td>
<td>1.09</td>
<td>R, Fe</td>
<td>pmC 105.22±0.30</td>
</tr>
<tr>
<td>Gel A</td>
<td>20096</td>
<td>1.11</td>
<td>R, Fe</td>
<td>—</td>
</tr>
</tbody>
</table>
Appendix B

A reference library for FTIR analysis of food crusts on pottery

FTIR spectra of different foodstuffs, raw and cooked, as well as their mixtures have been recorded. Both experimental and archaeological food crusts have been examined, before and after chemical pre-treatment. These spectra are collected here and will form the basis of a reference library, a collection of spectra of food crusts with known ingredients. Some of these spectra have been discussed in section 6.5.2.

The peaks in several spectra are marked with vertical lines to facilitate comparison. These are in some spectra additionally labelled with the respective wave numbers.

B.1 Raw ingredients
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

SID 13574
uncooked rocket

SID 13575
uncooked celery
B.1. RAW INGREDIENTS

SID 13576
uncooked roe deer meat

SID 13577
uncooked plaice
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

SID 13578
uncooked roach

SID 13579
uncooked cod
B.2 Cooked ingredients

SID 13868 vegetables:
1. sample, a) Brussels sprouts

Cooked vegetables
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

SID 13868 vegetables: 1. sample, b) Brussels sprouts

Cooked vegetables

SID 13878 cod + vegetables: cooked cod
B.2. COOKED INGREDIENTS

![Graph showing transmission spectra of uncooked and cooked cod](image1)

- Uncooked cod
- Cooked cod * 2.1

![Graph showing transmission spectrum of SID 13815 cooked cod and vegetables](image2)
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

Roach (freshwater fish), cooked with vegetables
- crust
- cooked and mixed with vegetables
- uncooked crust, upper rim
- cooked

Transmission (%)

827 787 719 667 550
3404 3078 2958 2852 2713
1745 1654 1542 1419 1381
1317 1240 1162 1094 874
787 750 667 550 3404

SID 13817
cooked roe deer meat and vegetables

Transmission (%)

50 45 40 35
3000 2500 2000 1500 1000 500 0
4000 3500 3000 2500 2000 1500 1000 500 0
4000 3500 3000 2500 2000 1500 1000 500 0
4000 3500 3000 2500 2000 1500 1000 500 0
4000 3500 3000 2500 2000 1500 1000 500 0
B.2. COOKED INGREDIENTS

SID 13819 roe deer + plaice, cooked meat

SID 13820 roe deer + plaice, cooked fish
Cooking and charring of roe deer meat and plaice.
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

SID 13887
roach and vegetables
cooked fish
B.3 Experimental food crusts

Base-soluble fraction (“humic”) of two wild boar food crust samples.
Roach food crust. Comparison of different pre-treatment fractions: Base-soluble (“humic”) vs. base-insoluble. Furthermore, comparison of two sub-samples from the same food crust, pre-treated individually (base-insoluble fraction from both, indicated by black and green lines).
B.3. EXPERIMENTAL FOOD CRUSTS

Cod and vegetables: different food crust samples
B.3. EXPERIMENTAL FOOD CRUSTS

SID 13888 roach and vegetables: 3. sample, upper rim

SID 13890 roe deer + vegetables crust
Roe deer and vegetables food crust. Comparison: four scans vs. 20 scans on the same tablet.

The same sample measured on different days, on different tablets.
Roe deer and plaice food crust.
APPENDIX B. FTIR SPECTRA OF FOOD CRUSTS

SID 13822 roe deer and plaice with crust

SID 13894 roe deer + plaice, crust
B.3. EXPERIMENTAL FOOD CRUSTS

![Graph 1](image1.png)

**SID 13893 roe deer + plaice sample from upper rim**

![Graph 2](image2.png)

**SID 13895 roe deer + plaice, crust**

**cm⁻¹**

**Transmission (%)**
B.4 Archaeological food crusts
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The hardwater effect in AMS 14C dating of food crusts on pottery

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\textsuperscript{c}Dezernat 5 (Süd) Außenstelle Neumünster, Archäologisches Landesamt Schleswig-Holstein, Gartenstraße 10, 24534 Neumünster, Germany

Abstract

The pottery investigated in this study comes from late mesolithic inland sites next to rivers in Northern Germany. The first AMS 14C datings of food crusts from these sites showed surprisingly high ages, which could be caused by the hardwater effect.

Modern samples from the rivers have ages of several hundred 14C years, and a modern food crust prepared from fish with a certain reservoir age shows the same age as the fish. Surprisingly, there was a large age difference between water samples and fish/mollusc shell from the same river. Associated archaeological samples of terrestrial and fluvial origin show age differences of several hundred and up to 3000 years. These high age differences are only to a limited extent transferred to the archaeological food crusts.

1. Introduction

Pottery is one of the most important materials for prehistoric archaeology and often used to define cultures and to study cultural contacts and developments. For relating the archaeological sequences to a calendar time scale, an accurate scientific dating of the pottery is essential. Radiocarbon dating of pottery is often possible when charred organic remains ("food crusts") are preserved on the pots, as these can be regarded contemporaneous to the usage of the pottery. Problems arise when the food crusts are affected by reservoir effects.

In the case of a reservoir with a different radiocarbon activity than the atmosphere, corrections of the initial radiocarbon activity have to be applied. Otherwise, spurious ages would be obtained. The effect the radiocarbon activity of a certain reservoir has on the radiocarbon age of a sample is called reservoir effect. There are different sources of 14C depleted carbon in freshwater environments. The most important is the dissolution of geologic carbonates. In this case, the freshwater reservoir effect is called hardwater effect. The water hardness is defined as the concentration of the alkaline earth metal ions, predominantly calcium and magnesium. They originate often from carbonates. The water hardness is therefore an indicator of the carbonate concentration and thus of the amount of 14C-dead material in the water. The hardwater effect is expected to be greater in running water (rivers), than in stagnant water (lakes). If there is not a noticeable meltwater component, river water consists largely of groundwater [8].

The effect of dissolved bicarbonates on the radiocarbon age has been anticipated very early, when Godwin [4] examined dates from British lake deposits. The occurrence of the hardwater effect on food crusts on pottery was first proposed in 2003 [5].

2. Measurements and results

The sites analysed in this work are shortly occupied hunting stations from the Ertebølle culture. The archaeological period of...
pretreated sample, using continuous flow (EA–CF), yielding both Kayhude, Alster and Schlamersdorf, Trave – archaeological samples. The fishbones from both sites are much older than the other samples, and none of the food crusts is as old as

Table 2

| Lab no. | Sample material | pmC | ¹⁴C age (year BP) | Reservoir age (year) | ¹³C % w.r.t. VPDB | Δ¹³C
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alter</td>
<td>Water</td>
<td>78.28 ± 0.32</td>
<td>1966 ± 33</td>
<td>2449 ± 45</td>
<td>−14.06 (DI)</td>
<td>−13.59 (DI)</td>
</tr>
<tr>
<td>11461</td>
<td>Snail-shell</td>
<td>94.75 ± 0.37</td>
<td>433 ± 32</td>
<td>868 ± 47</td>
<td>−15.36 (DI)</td>
<td>−25.29 (EA)</td>
</tr>
<tr>
<td>11462</td>
<td>Fishbone</td>
<td>97.27 ± 0.35</td>
<td>222 ± 29</td>
<td>653 ± 46</td>
<td>−25.46 (DI)</td>
<td>−25.46 (DI)</td>
</tr>
<tr>
<td>Trave</td>
<td>Water</td>
<td>86.54 ± 0.57</td>
<td>170 ± 55</td>
<td>1631 ± 63</td>
<td>−13.59 (DI)</td>
<td>−13.59 (DI)</td>
</tr>
<tr>
<td>11394</td>
<td>Fishbone (fresh)</td>
<td>96.51 ± 0.38</td>
<td>284 ± 32</td>
<td>722 ± 47</td>
<td>−26.00 (EA)</td>
<td>15.02</td>
</tr>
<tr>
<td>11396</td>
<td>Fishbone (cooked)</td>
<td>97.00 ± 0.34</td>
<td>244 ± 28</td>
<td>679 ± 41</td>
<td>−24.30 (EA)</td>
<td>15.66</td>
</tr>
<tr>
<td>11414</td>
<td>Food crust (fish)</td>
<td>96.11 ± 0.31</td>
<td>371 ± 23</td>
<td>756 ± 41</td>
<td>−28.14 (EA)</td>
<td>18.08</td>
</tr>
<tr>
<td>11411</td>
<td>Food crust (boar meat)</td>
<td>106.87 ± 0.45</td>
<td>−537 ± 34</td>
<td>−17.84 (EA)</td>
<td>7.91</td>
<td></td>
</tr>
</tbody>
</table>

14C datings and stable isotope values of modern samples. Note that the water samples are much older than the fishbones from the same rivers, and that even the snail-shell is

Table 1

| Lab no. | Sample material | pmC | ¹³C age (year BP) | Reservoir age (year) | ¹³C % w.r.t. VPDB | Δ¹³C
<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
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<td>86.54 ± 0.57</td>
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<tr>
<td>11394</td>
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<td>96.51 ± 0.38</td>
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<td>−26.00 (EA)</td>
<td>15.02</td>
</tr>
<tr>
<td>11396</td>
<td>Fishbone (cooked)</td>
<td>97.00 ± 0.34</td>
<td>244 ± 28</td>
<td>679 ± 41</td>
<td>−24.30 (EA)</td>
<td>15.66</td>
</tr>
<tr>
<td>11414</td>
<td>Food crust (fish)</td>
<td>96.11 ± 0.31</td>
<td>371 ± 23</td>
<td>756 ± 41</td>
<td>−28.14 (EA)</td>
<td>18.08</td>
</tr>
<tr>
<td>11411</td>
<td>Food crust (boar meat)</td>
<td>106.87 ± 0.45</td>
<td>−537 ± 34</td>
<td>−17.84 (EA)</td>
<td>7.91</td>
<td></td>
</tr>
</tbody>
</table>

The economy of the Ertebølle culture is Mesolithic (hunting, gathering and fishing), some aspects of a Neolithic way of life had been adopted. This includes the use of pottery, a tendency towards sedentarity and possibly the first domesticated animals. The pottery examined in this study is believed to be the first pottery that was made in Northern Germany. The rivers in the study area contain hard (carbonate-rich) water, so that a hardwater effect is expected.

Modern water samples, fish, and food crusts on pottery have been radiocarbon dated to determine the possibility and order of magnitude of the freshwater effect. Water dating was done on the DIC. Fish dates were obtained from the bone collagen. Archaeological food crusts as well as associated samples of terrestrial and fluvial origin have been dated. If applicable, the same sample preparation methods were used for both sample categories, modern and archaeological. The results of the radiocarbon datings are presented in Tables 1 and 2.

With F being the fraction modern carbon of the riverine sample and F₀ the corresponding value of the terrestrial sample, the reservoir effect Δt can be calculated as

$$Δt = \tau (\ln F_0 - \ln F) = \tau \ln \frac{F_0}{F}.$$ (1)

If the reservoir age is to be expressed in radiocarbon years, the conventional mean life 8033 a belonging to Libby’s radiocarbon half-life has to be taken. For an estimation of the reservoir effect in calendar years, the mean life of 8267 a belonging to the physical half-life of radiocarbon, 5730 a, is used.

Table 2

| Lab no. | Sample material | ¹³C age | Date calender BC (95.4%) | ¹³C % w.r.t. VPDB | Δ¹³C
<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td>Alter</td>
<td>Food crust</td>
<td>5692 ± 54</td>
<td>4690 — 4734</td>
<td>−29.80 (EA)</td>
<td>6.51</td>
</tr>
<tr>
<td>11403</td>
<td>Food crust (humic)</td>
<td>6748 ± 160</td>
<td>5984 — 5379</td>
<td>−28.74 (EA)</td>
<td>11.28</td>
</tr>
<tr>
<td>11404</td>
<td>Food crust</td>
<td>6088 ± 56</td>
<td>5209 — 4849</td>
<td>−28.90 (DI)</td>
<td>1.78</td>
</tr>
<tr>
<td>11479</td>
<td>Food crust</td>
<td>5349 ± 106</td>
<td>4443 — 3960</td>
<td>−26.53 (EA)</td>
<td>24.83 (DI)</td>
</tr>
<tr>
<td>11480</td>
<td>Charcoal</td>
<td>5437 ± 41</td>
<td>4359 — 4178</td>
<td>−22.41 (DI)</td>
<td>27.74 (DI)</td>
</tr>
<tr>
<td>11695</td>
<td>Fishbone (pike)</td>
<td>8514 ± 83</td>
<td>7734 — 7369</td>
<td>−22.41 (DI)</td>
<td>7.91</td>
</tr>
<tr>
<td>Trave</td>
<td>Wildcat</td>
<td>5685 ± 60</td>
<td>4687 — 4371</td>
<td>−19.16 (EA)</td>
<td>6.60</td>
</tr>
<tr>
<td>11398</td>
<td>Beaver</td>
<td>6480 ± 90</td>
<td>5618 — 5303</td>
<td>−22.54 (EA)</td>
<td>4.68</td>
</tr>
<tr>
<td>11400</td>
<td>Wild boar</td>
<td>6035 ± 60</td>
<td>5206 — 4780</td>
<td>−22.42 (DI)</td>
<td>5.01</td>
</tr>
<tr>
<td>11407</td>
<td>Burnt wood</td>
<td>5750 ± 90</td>
<td>4796 — 4371</td>
<td>−23.63 (DI)</td>
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</tr>
<tr>
<td>11476</td>
<td>Red deer</td>
<td>6275 ± 65</td>
<td>5461 — 5047</td>
<td>−23.54 (DI)</td>
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<tr>
<td>11481</td>
<td>Food crust</td>
<td>6850 ± 120</td>
<td>5987 — 5559</td>
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</tr>
<tr>
<td>11482</td>
<td>Outer crust</td>
<td>5190 ± 110</td>
<td>4321 — 3715</td>
<td>−28.01 (EA)</td>
<td>6.36</td>
</tr>
<tr>
<td>11483</td>
<td>Food crust</td>
<td>5590 ± 110</td>
<td>4707 — 4217</td>
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<td>9.39</td>
</tr>
<tr>
<td>11484</td>
<td>Plant rest from sherd</td>
<td>5985 ± 50</td>
<td>4999 — 4729</td>
<td>−27.36 (EA)</td>
<td>5.12</td>
</tr>
<tr>
<td>11484</td>
<td>Food crust</td>
<td>5830 ± 180</td>
<td>5207 — 4344</td>
<td>−27.46 (EA)</td>
<td>19.49</td>
</tr>
<tr>
<td>11842</td>
<td>Fishbone</td>
<td>7640 ± 65</td>
<td>6631 — 6398</td>
<td>−26.78 (DI)</td>
<td>19.49</td>
</tr>
<tr>
<td>11844</td>
<td>Fishbone</td>
<td>7620 ± 110</td>
<td>6679 — 6237</td>
<td>−19.49</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Calibrated ages of samples from Kayhude, Alster and Schlamersdorf, Trave. The age ranges of terrestrial and fluvial samples are marked with shading, and food crust dates are marked with pictures of Ertebølle pottery. (a) Kayhude, (b) Schlamersdorf.
2.1. Modern samples

In the case of recent samples, \( F_0 \) is the fraction modern carbon of the atmosphere at the moment of collecting the samples from the river (Summer 2007). The relevant atmospheric radiocarbon concentration, measured in southern Germany and Switzerland, was between 105 and 105.5 pmC (pers. comment Bernd Kromer).

Modern reservoir ages are only estimates because of the unknown influence the bomb pulse had on the carbon entering the river. Table 1 shows the dating results and reservoir ages for both rivers. The DIC of the river water has a radiocarbon age of 1966 (Alster) and 1170 (Trave) radiocarbon years, which results in estimated reservoir ages of about 2450 and 1630 calendar years, respectively.

In contrast to that, fishbones from recent fish have radiocarbon ages of 220 (Alster) and 280 (Trave) radiocarbon years and estimated reservoir ages of 650 (Alster) and 720 (Trave) calendar years. There are several possible explanations for the age differences between water and fish. Firstly, the fish caught for our studies, the common roach/Rutilus rutilus, could partly feed on terrestrial food sources (surface insects or terrestrial material that is washed into the river?), and not only on water animals and water plants. Secondly, the water dating only represents a snapshot of the water’s radiocarbon age at the moment of sampling, while the fishbone radiocarbon age is integrated over the time of bone formation. It is possible that the reservoir age of the water varies with season or weather conditions like amount of rainfall. Thirdly, we only measured DIC, and not the reservoir age of the total carbon available to the fish.

As the main study material are archaeological food crusts on pottery, not only water and fish have been analysed, but also recent food crusts. For this purpose, two food crusts have been prepared: One from the roach, and one from wild boar as a terrestrial food crust for identifying the former ingredients of the meals cooked in the stone age vessels. The wild boar food crust had a radiocarbon age of \(-540 \) radiocarbon years BP (see Table 1), out of the range of the used calibration curve “Kueppers et al.” [7]. The curve was extended to present using an exponential decay curve. The calibrated age of the wild boar food crust is \(3 \pm 2\) years. An age like this was expected, since the incorporation of atmospheric CO\(_2\) takes about one year, and as the meat which was bought frozen in July most likely came from a wild boar that was killed in the autumn before. The wild boar’s \(\delta^{13}C\) value shows that it was fed with C4-plants (probably maize), which did not play a role in the nutrition of archaeological wild boars from that area. The fish food crust has a radiocarbon age of 370 \(^{14}C\) years BP and its reservoir age is estimated to 760 calendar years. It has thus the same age as the bones of the fish from which the crust has been made.

2.2. Archaeological samples

Table 2 shows the radiocarbon determinations on archaeological material. They were calibrated with OxCal [1,2] using the terrestrial calibration curve IntCal04 [9]. In Fig. 1, the calibrated ages of the samples can be seen. The age ranges of terrestrial and fluvial samples are marked with shading, and food crust dates are marked with pictures of Ertebølle pottery.

There is a remarkable age difference between fishbone samples and terrestrial samples for both sites. In Schlamersdorf, there is a big variability of terrestrial ages, which might be caused by the unsure stratigraphy. Being situated close to rivers, both sites were repeatedly inundated, and no clear stratigraphy could be seen. However, the fishbone dates are significantly older than the terrestrial samples. At both sites, the food crust samples have the same or higher ages than the terrestrial samples. None of the food crusts is as old as the fishbones. If one assumes that the food crusts and fishbones were contemporary, it would mean, that the food crusts are not exclusively made from fish but from a mixture of freshwater fish and terrestrial ingredients. The \(\delta^{13}C\) values indicate a significant freshwater component, but terrestrial plants cannot be ruled out either. \(\delta^{15}N\) values can apparently not be used for the identification of the ingredients, as some food crusts even had negative \(\delta^{15}N\) values. It is not yet clear which mechanism causes these unusual \(\delta^{15}N\) values.

3. Future plans

The hardwater effect in the rivers Alster and Trave will be monitored by analysing water samples that will regularly be taken throughout the next year. This will show if the very high reservoir ages were exceptional, or if the reservoir ages generally are high in these rivers. Additionally, DOC and more organic samples from the rivers like plants, fish and molluscs will be collected. The water plants should show reservoir ages that are integrated over the whole growth period of the plants, whereas fish show integrated reservoir ages of all their food sources. This will hopefully explain the age difference we measured between the roach and the water. \(^{14}C\) and stable isotopes will be measured on food crusts produced from plants and from different mixtures of fish, terrestrial meat and plants. Other analysis methods will also be tested. The aim is to find a method that can be applied to the archaeological food crusts for identifying the former ingredients of the meals cooked in the stone age vessels.

References

Ertebølle Cuisine: A freshwater radiocarbon reservoir effect in Mesolithic food crusts from Northern Germany

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Introduction
Pottery is one of the most important materials for prehistoric archaeology and is often used to define cultures and to study cultural contacts and developments. It was also a remarkable innovation for Terminal Mesolithic “cuisine”: Boiling in vessels over direct heat made food resources available that otherwise were indigestive, whilst preserving all nutrients in the liquid.
For reliable $^{14}$C dating of food crusts on pottery, reservoir effects have to be ruled out or quantified. It is thus important to find out whether the food crust contains components of marine or freshwater resources.

The food crusts analysed in this study are from pottery found in Schleswig-Holstein, Northern Germany, belonging to the Terminal Mesolithic Ertebølle Culture. This hunter-gatherer culture was the first culture in Northern Germany, Poland and Southern Scandinavia that adopted pottery production.

$^{14}$C datings of food remains in pottery from two inland sites resulted in ages more than 500 years older than those from coastal settlements (Hartz 1996, Clausen 2008) so that a reservoir effect was suspected (Hartz and Lübke 2006). The two sites are Schlammersdorf LA 5 on the river Trave and Kayhude LA 8 on the river Alster (Hartz 1997, Clausen 2008); both rivers are characterised by hard water. Remains of fish and fishing gear had been excavated at these sites and the consumption of freshwater fish is typical for the Late Mesolithic, so it is probable that freshwater fish was cooked in the pots.

Modern samples (water, plants and animals) from both rivers were collected in 2007-2009 and $^{14}$C dated to determine whether a reservoir effect in that area is likely, and of what magnitude it could be. Food crusts from different ingredients and mixtures of ingredients were analysed to find the relation between the isotopic values of the ingredients and of the food crust. The reservoir ages of ingredients and food crusts were compared as well.
In order to quantify the effect on ancient material, archaeological samples of terrestrial and freshwater origin as well as archaeological food crusts have been $^{14}$C dated.

Radiocarbon dating and reservoir effects
A terrestrial sample’s carbon derives from the atmosphere. When a sample obtains its carbon from a reservoir with a lower $^{14}$C concentration than the atmosphere, too high $^{14}$C ages will be obtained. The difference between the $^{14}$C age of a sample from such a reservoir and the $^{14}$C age of a contemporaneous terrestrial sample is called the reservoir age.
A marine reservoir age of 400 years is common for Danish and northern German coastal areas, as well as for most of the North Atlantic region (Tauber 1979; Heier-Nielsen et al. 1995). Another example of a reservoir effect is the hard water effect (Godwin 1951, Deevey et al. 1954). Hard water contains considerable amounts of $^{14}$C dead carbon: dissolved carbonate from rocks and deposits in the underground has infinite ages on the $^{14}$C timescale. The initial $^{14}$C concentration of an organism living in hard water is thus lower than that of a terrestrial sample (Clark and Fritz 1997, Fontes and Garnier 1979). The hardwater effect can lead to potentially very high reservoir ages, also in humans who eat fish from hard water (Cook et al. 2001; Smits and van der Plicht 2009; Olsen et al. 2010). A hardwater effect in food crusts on pottery was first proposed by Fischer and Heinemeier (2003), and for example found by Boudin et al. (in press) to be $320\pm160$ $^{14}$C years for Swifterbant pottery from Belgium.

**Stable isotope analysis**

Both carbon and nitrogen have two naturally occurring stable isotopes: $^{12}$C, $^{13}$C and $^{14}$N, $^{15}$N. The mass difference between isotopes leads to different chemical reaction rates. “Isotopic fractionation” is the enrichment or depletion of a certain isotope during a chemical reaction or physical or biological process. Stable isotope contents are expressed as rare/abundant ratios ($^{13}$C/$^{12}$C and $^{15}$N/$^{14}$N), relative to this ratio for a standard, expressed as delta values ($\delta^{13}$C and $\delta^{15}$N) in permil deviation, for example $\delta^{13}$C = ($^{13}$R$_{sam}$ – $^{13}$R$_{std}$) / ($^{13}$R$_{std}$) * 1000‰. The standards for $^{13}$C and $^{15}$N are VPDB and AIR, respectively (Craig 1957; Mariotti 1983).

$^{13}$C can be used to differentiate between marine and terrestrial food sources as the food chains in these environments begin with different $^{13}$C/$^{12}$C ratios. Atmospheric CO$_2$ has $\delta^{13}$C ≈ -7‰, marine CO$_2$ has $\delta^{13}$C ≈ 0‰ because of fractionation in the CO$_2$ exchange across the air-water boundary. The type of photosynthesis (C3) that is used by water plants and most plants in temperate Europe leads to a fractionation of about -18‰. Terrestrial plants thus have $\delta^{13}$C ≈ -25‰, marine plants ≈ -18‰. There is a shift of about +5‰ from food source to consumer bone collagen. Humans who live mainly on marine food, have $\delta^{13}$C values in their bone collagen of about -13‰ (Lanting and van der Plicht 1995/6, Arneborg et al. 1999). A predominantly terrestrial diet leads to $\delta^{13}$C ≈ -21‰ in bone collagen.

In the case of $^{15}$N, there is enrichment of about 3‰ with each step in trophic level (Ambrose 2001). In aquatic systems, food chains are generally longer than in terrestrial systems, resulting in more $^{15}$N enrichment steps. Humans who live on a 100% aquatic diet may have $\delta^{15}$N = 16-18‰ in their bone collagen (Schoeninger et al. 1983, Cook et al. 2001).

Thus, the combination of $\delta^{13}$C and $\delta^{15}$N values could in principle be used to identify the ingredients of a food crust: $^{13}$C differentiates marine and terrestrial (including freshwater) systems, whereas $^{15}$N differentiates between water (including freshwater) and land. A combined measurement is thus needed to identify freshwater samples. The identification of a sample's origin can be used to correct a $^{14}$C measurement for the reservoir effect (Arneborg et al. 1999, Cook et al. 2001). Obvious difficulties are,
however, identifying individual food components in a mixture as well as fractionation in the charring of food crusts.

**Methods**
For the dating of water samples, dissolved inorganic carbon (DIC) was extracted as CO$_2$ and reduced to graphite for radiocarbon dating (Boaretto et al. 1998). Some water plants from the rivers have been analysed as an example for the first step in the food chain. Fish, shells and a crayfish have also been examined. Bulk samples were analysed, but in the case of fishbone, only the collagen fraction was used.

It has been tested whether the $^{14}$C age of a food crust is the same as that of the cooking ingredients. One could imagine that the process of cooking and scorching leads to effects that alter the $^{14}$C age (e.g. contamination), so both ingredients and food crusts have been $^{13}$C dated. The stable isotope ratios $\delta^{13}$C and $\delta^{15}$N were also measured for these samples. The food crusts were produced in copies of Stone Age pottery made using prehistoric methods (see Philippsen (2010) for details).

From the archaeological sites, terrestrial samples, fishbones and food crusts were analysed. Fish crusts, wood and charcoal samples were pretreated with the method described in Olsson (1976). Collagen from bones and fishbones was extracted with a modified Longin-method and purified by ultrafiltration (Longin 1971; Brown et al. 1988; Jørgkov et al. 2007; Kanstrup 2008).

The pretreated samples were combusted to CO$_2$. Part of it could be used for $\delta^{13}$C measurements on a GV Instruments IsoPrime stable isotope mass spectrometer. A fraction corresponding to 1 mg carbon was converted to graphite by reduction with H$_2$ in the presence of a cobalt catalyst. A fraction of pretreated bone and food crust samples was measured directly on the mass spectrometer, yielding both $\delta^{13}$C and $\delta^{15}$N.

AMS $^{14}$C measurements were carried out using the EN tandem accelerator at Aarhus University. The dating results are reported according to international convention (Stuiver and Polach 1977) as conventional $^{14}$C dates in $^{14}$C yr BP (before AD 1950) based on the measured $^{14}$C/$^{13}$C ratio corrected for the natural isotopic fractionation by normalizing the result to the standard $\delta^{13}$C value of $–25\%$ PDB (Andersen et al. 1989).

The radiocarbon determinations on archaeological material were calibrated with OxCal v4.1.4 (Bronk Ramsey 2009) using the terrestrial calibration curve IntCal09 (Reimer et al. 2009).

**Results and discussion**

*Stable isotopes*
Figure 1 shows the stable isotope results of the experimental and archaeological food crusts. In some cases, different samples from the same pot have very different stable isotope values. Several measured values differ a lot from the expected values that are calculated from the relative contributions of the ingredients to the carbon and nitrogen of the food crust. This is quite obvious when one bears in mind that the meals were not totally homogenised before they scorched. The potsherd analysed may thus not be representative of the meal prepared in the pot.
The $\delta^{13}C$ value of the wild boar food crust is much less negative than expected. This wild boar was probably fed with maize which is a C4 plant with very different $\delta^{13}C$ values (ca. -13‰).

The $\delta^{13}C$ values of the archaeological food crusts from Schlamersdorf and Kayhude are comparable to those found by Fischer and Heinemeier (2003) and Smits and van der Plicht (2009): they range between -29 and -27‰, indicating terrestrial to freshwater origin. The $\delta^{15}N$ values span a range of 3 to 13‰. $\delta^{15}N$ values in archaeological food crusts, especially in those from Schlamersdorf, are lower than those in experimental food crusts. Maybe these values can be used for a characterisation of the preservation status of a potsherd food crust. Further studies are needed to develop reliable criteria for this effect.

$^{14}C$ dating

Modern samples
Table 2 shows the broad range of $^{14}C$ ages for modern samples. It is evident that there is no uniform reservoir age for the water, plants or animals from the same river. Recent terrestrial samples have negative $^{14}C$ ages, caused by the increase of atmospheric $^{14}C$ concentration due to nuclear bomb tests since the late 1950s (Fischer and Heinemeier 2003). The crust made of a roach, caught in 2007, with a $^{14}C$ age of 285 ± 30 BP, had a $^{14}C$ age of 330±20 BP. Similarly, the wild boar food crust has no age offset, as expected for a modern terrestrial sample. We can thus conclude that ingredients and crust have the same reservoir age.

Archaeological samples
The terrestrial age range of Schlamersdorf (figure 2) complies with earlier charcoal datings from this site (Hartz 1993). The broad range of terrestrial ages, probably caused by uncertainties in the stratigraphy, makes it difficult to calculate reservoir ages. It is obvious, though, that fishbones are significantly older than other samples. Three food crusts had earlier been dated to around 5300 cal. BC (Hartz 1996); their $\delta^{13}C$ values between -28.6 and -31.9‰ indicate freshwater ingredients. Two of the three food crusts we radiocarbon dated from that site are from 4000-5000 BC, and one was from 5600-6000 BC. An interesting case is the potsherd AAR-11481 where both inner and outer crust have been dated. If one assumes that the outer crust is soot from the cooking fire, then it should give the date of cooking, or an older date in case old wood had been used. The reservoir effect would, in this case, be approximately 2000 years. As this outer crust is younger than all the other terrestrial samples, we will examine it more closely to find out if it really is soot, or just some younger contamination. In one of the sherds, AAR-11483, we were lucky to find some plant remains that presumably had been incorporated in the clay during the forming of the pottery. Unfortunately, the food crust sample of AAR-11483 was lost during dating.

In Kayhude, the samples were collected from a relatively undisturbed stone paving (pers. comm. I. Clausen, 2007). The age difference of over 3000 years between the fish and the
charcoal from Kayhude is much larger than the reservoir ages that we find for modern fish, but of the same order of magnitude as the reservoir age for modern water and plants. None of the food crusts are as old as the fishbones, though. The humic fraction of two food crusts has also been dated. The humic fraction is likely to consist of humic acids from the soil, and is thus removed from the samples. Here it is older than the food crusts (figure 3), indicating contamination with an older soil substance.

The hardwater effect at Schlamersdorf and Kayhude seems to be larger than the effect reported by Fischer and Heinemeier (2003), at least for the fishbones. In their study area, the Åmose on Zealand, Denmark, the fish was 100 to 500 $^{14}$C years older than the archaeological context, while the food crusts were up to 300 $^{14}$C years older.

**Conclusion and Future Plans**

According to our results, a reservoir effect of a few hundred and up to a few thousand years seems possible in the pottery from Schlamersdorf and Kayhude. The large variability in ages leads to a high variability in the estimated reservoir age and thus to a broad range of the estimated “real” age of the pottery of, e.g. 5300 to 4500 BC. The dating of 4750 BC for coastal Ertebølle pottery is most likely too old as its $\delta^{13}$C value of -20‰ indicates a large marine component (Hartz and Lübke 2006), and we assume a later introduction of pottery to the coastal sites of Schleswig-Holstein. The pottery from these inland sites can thus be older, equally old or even younger than the pottery from coastal sites.

With the broad age range for the oldest pottery in Schleswig-Holstein, several cultures come into consideration as the source of this innovation. Import finds show connections between the Ertebølle culture and fully neolithic cultures to the south and east of the river Elbe (cf. Hartz and Glykou 2008), which are thus a possible source of ceramic knowledge. Interestingly, other Late Mesolithic groups throughout Northern Europe produced pottery, often quite similar to the typical pointed-based pots of the Ertebølle culture (see table 4), so that the origin of Ertebølle pottery is not necessarily a Neolithic culture. The eastern Baltic (pottery from around 5000 BC), or the Netherlands and Belgium (from around 4700 BC) could have been the regions of origin.

The stable isotope ratios $\delta^{13}$C and $\delta^{15}$N are only suitable to a limited extent for identification of the ingredients of a food crust. The hardwater effect can lead to varying and possibly very high $^{14}$C age offsets. Thus, $^{14}$C dates of such samples should be treated with extreme caution. Radiocarbon dating of the experimental food crusts is in progress. We hope to find a correlation between the stable isotope values and the $^{14}$C age of a certain sample of a food crust.

**Acknowledgements**

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References


Figure 1: Stable isotope values of experimental and archaeological food crusts. The data of experimental food crusts are marked with the names of the ingredients. The data of archaeological food crusts are marked with the name of the site. Neustadt is a coastal site so that marine fish is one possible ingredient for this food crust.

Figure 2: Radiocarbon dating of archaeological samples from Schlamersdorf. The age ranges of fresh-water and terrestrial samples are shaded and radiocarbon datings of food crusts on pottery are coloured red. There is a big variability of terrestrial ages, which might be caused by the unsure stratigraphy. The fishbones are significantly older than the terrestrial samples. The food crust dates are within the ages of terrestrial samples or slightly older. One striking example is the potsherd AAR-11481 where both inner and outer crust have been dated. The large age difference between those makes a reservoir effect very likely.

Figure 3: Radiocarbon dating of archaeological samples from Kayhude. The age ranges of fresh-water and terrestrial samples are shaded and radiocarbon datings of food crusts on pottery are coloured red. The samples were taken from a stone paving that seemed to be relatively undisturbed, so that it is likely here that all dated samples were contemporaneous. The fishbones are significantly older than the terrestrial samples. The food crusts have the same apparent age as the terrestrial sample or are older, though none of the food crusts is as old as the fishbone.
R_Date AAR-11398 wildcat
R_Date AAR-11399 beaver
R_Date AAR-11400 wild boar
R_Date AAR-11402 wood
R_Date AAR-11405 wood
R_Date AAR-11406 wood
R_Date AAR-11407 wood
R_Date AAR-11408 wood
R_Date AAR-11476 red deer (a)
R_Date AAR-11476 red deer (b)
R_Date AAR-11481 outer crust
R_Date AAR-11481 inner crust
R_Date AAR-11482 food crust
R_Date AAR-11483 plant rests from sherd
R_Date AAR-11484 food crust
R_Date AAR-11842 fishbone
R_Date AAR-11844 fishbone

Calibrated date (calBC)

terrestrial samples

freshwater fish
OxCal v4.1.4 Bronk Ramsey (2010); r:5 Atmospheric data from Reimer et al (2009):

- R_Date AAR-11403 food crust
- R_Date AAR-11403 food crust humic fraction
- R_Date AAR-11404 food crust
- R_Date AAR-11404 food crust humic fraction
- R_Date AAR-11479 food crust
- R_Date AAR-11480 charcoal
- R_Date AAR-11695 fishbone (pike)

Calibrated date (calBC)

11000 10000 9000 8000 7000 6000 5000 4000

Freshwater fish
Terrestrial sample
Table 1: Food crust experiments with mixed ingredients. For each stew, the ingredients are listed. $\delta^{13}$C and $\delta^{15}$N values are given for the uncooked ingredients. From the relative amounts of the ingredients and their respective carbon and nitrogen content, an expected value for the homogeneous mixture was calculated. Different samples of the food and food crusts were taken. "Crust" denotes a random sample from the inside of the pot, which ingredients were unidentifiable – just what you would find on an archaeological potshard. Two other food crusts were made of only one ingredient each: freshwater fish (roach) and wild boar meat. The results for these two are given in table 2.

<table>
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<th>$\delta^{15}$N AIR (‰)</th>
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<td>Cooked mixture</td>
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<td>-30.27</td>
<td>9.02</td>
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<td>Chard</td>
<td>90</td>
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<td>-26.24</td>
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<td>11.42</td>
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<td>Cooked fish</td>
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<td>-18.61</td>
<td>13.96</td>
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<tr>
<td>Cooked meat</td>
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<td>-26.03</td>
<td>8.24</td>
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<td>Boiled over (froth)</td>
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<td>Crust (with fish and meat)</td>
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<td>Crust (upper rim)</td>
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<td>Crust 1</td>
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<td>13.94</td>
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<td>Crust 2</td>
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<td>-19.42</td>
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<td>Crust 3</td>
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<td></td>
<td>-21.14</td>
<td>11.89</td>
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</table>
Table 2: $^{14}$C and stable isotope measurements of modern samples. The water plants and animals were collected live in 2007 and 2008. “˚dH” for the water samples denotes the carbonate hardness, estimated with an aquarium test kit and expressed in German degrees (1˚dH = 17.848 milligrams of calcium carbonate per litre of water). Recent samples that are not influenced by a reservoir effect (terrestrial samples) have negative $^{14}$C ages in the order of magnitude of that of the wild boar food crust. The negative $^{14}$C ages are caused by the increase of atmospheric $^{14}$C concentration due to nuclear bomb tests since the late 1950s (Fischer et al. 2003). $\delta^{13}$C values marked with DI were measured on sample CO$_2$, while those marked with EA were measured on the pretreated samples.

<table>
<thead>
<tr>
<th>Lab No.</th>
<th>River</th>
<th>Sample type</th>
<th>$^{14}$C Age (uncal. Yr BP)</th>
<th>$\delta^{13}$C (%o wrt VPDB)</th>
<th>$\delta^{15}$N (%o wrt AIR)</th>
<th>misc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>11780</td>
<td>Trave</td>
<td>Water (Aug 07)</td>
<td>1170±55</td>
<td>-13.59 (DI)</td>
<td>7.5˚dH</td>
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<td>12882</td>
<td>Trave</td>
<td>Water (Sep 08)</td>
<td>1992±44</td>
<td>-11.30 (DI)</td>
<td>7.5˚dH</td>
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</tr>
<tr>
<td>13611</td>
<td>Trave</td>
<td>Water (Feb 09)</td>
<td>1176±33</td>
<td>-8.94 (DI)</td>
<td>8.0˚dH</td>
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<tr>
<td>11779</td>
<td>Alster</td>
<td>Water (Aug 07)</td>
<td>1967±33</td>
<td>-14.96 (DI)</td>
<td>5.0˚dH</td>
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<tr>
<td>12881</td>
<td>Alster</td>
<td>Water (Sep 08)</td>
<td>2619±48</td>
<td>-10.92 (DI)</td>
<td>4.5˚dH</td>
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<tr>
<td>13612</td>
<td>Alster</td>
<td>Water (Feb 09)</td>
<td>1521±35</td>
<td>-14.85 (DI)</td>
<td>5.0˚dH</td>
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<td>12870</td>
<td>Trave</td>
<td>Underwater plant</td>
<td>-74±35</td>
<td>-25.42 (EA)</td>
<td>9.22</td>
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<tr>
<td>12871</td>
<td>Trave</td>
<td>Water plant</td>
<td>879±37</td>
<td>-28.67 (EA)</td>
<td>13.67</td>
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<tr>
<td>12872</td>
<td>Trave</td>
<td>Underwater plant</td>
<td>1700±55</td>
<td>-17.65 (EA)</td>
<td>8.50</td>
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<tr>
<td>11394</td>
<td>Trave</td>
<td>Fishbone (roach)</td>
<td>285±32</td>
<td>-26.00 (EA) -25.91 (DI)</td>
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<tr>
<td>12875</td>
<td>Trave</td>
<td>Fish (spined loach)</td>
<td>1664±39</td>
<td>-27.18 (EA)</td>
<td>17.88</td>
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<tr>
<td>12876</td>
<td>Trave</td>
<td>Crayfish</td>
<td>1365±40</td>
<td>-23.65 (EA)</td>
<td>11.54</td>
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<td>12873</td>
<td>Alster</td>
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<td>2273±41</td>
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<td>14.26</td>
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<td>11414</td>
<td>Trave</td>
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<td>-28.13 (EA) -30.47 (DI)</td>
<td>13.30</td>
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<tr>
<td>11411</td>
<td>(Trave)</td>
<td>Wild boar food crust</td>
<td>-535±55</td>
<td>-17.88 (EA) -18.03 (DI)</td>
<td>8.13</td>
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Table 3: Radiocarbon dating and stable isotope measurements of archaeological samples from Kayhude LA 8 and Schlamersdorf LA 5, Schleswig-Holstein, Northern Germany. $\delta^{13}C$ values marked with DI were measured on sample CO$_2$, while those marked with EA were measured on the pretreated samples with the mass spectrometer in combination with an elemental analyser. From a red deer bone, two samples have been extracted and pretreated individually to illustrate the variation in radiocarbon dates of samples that have precisely the same “real” age. Note sample AAR-11481 where both the inner and outer crust of a potsherd have been dated, resulting in a large age difference. In sherd AAR-11483, both a food crust and a plant rest inside the clay were found. Unfortunately, the carbon extracted from the food crust was lost during dating.

<table>
<thead>
<tr>
<th>Lab no. AAR</th>
<th>Name and Material</th>
<th>$^{14}C$ age Yr BP</th>
<th>cal. age BC (95.4%)</th>
<th>$\delta^{13}C$ (%o wrt VPDB)</th>
<th>$\delta^{15}N$ (%o wrt AIR)</th>
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<td><strong>Kayhude (Alster)</strong></td>
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<tr>
<td>11403</td>
<td>Food crust</td>
<td>5695±55</td>
<td>4690-4370</td>
<td>-28.38 (EA)</td>
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<tr>
<td>11403</td>
<td>Food crust, humic fraction</td>
<td>6740±160</td>
<td>5980-5380</td>
<td>-28.90 (DI)</td>
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<tr>
<td>11404</td>
<td>Food crust</td>
<td>6090±55</td>
<td>5210-4850</td>
<td>-28.90 (EA)</td>
<td>12.54</td>
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<tr>
<td>11404</td>
<td>Food crust, humic fraction</td>
<td>6420±65</td>
<td>5610-5320</td>
<td>-28.90 (DI)</td>
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<tr>
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<td>4440-3960</td>
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<tr>
<td>11480</td>
<td>Charcoal</td>
<td>5437±41</td>
<td>4360-4180</td>
<td>-24.83 (DI)</td>
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<td>11695</td>
<td>Fishbone</td>
<td>8514±83</td>
<td>7730-7370</td>
<td>-22.41 (DI)</td>
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<td><strong>Schlamersdorf (Trave)</strong></td>
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<td>11398</td>
<td>Wildcat</td>
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<td>4690-4370</td>
<td>-19.16 (EA)</td>
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<td>11399</td>
<td>Beaver</td>
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<td>-22.54 (EA)</td>
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<td>11400</td>
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<tr>
<td>11408</td>
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<td>4580-4360</td>
<td>-27.47 (DI)</td>
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<tr>
<td>11476</td>
<td>Red deer (a)</td>
<td>6275±65</td>
<td>5460-5050</td>
<td>-23.63 (DI)</td>
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<tr>
<td>11481</td>
<td>Food crust</td>
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<td>5990-5560</td>
<td>-27.23 (EA)</td>
<td>3.95</td>
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<tr>
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<td>Outer crust</td>
<td>5190±110</td>
<td>4320-3710</td>
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<td>3.95</td>
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<td>Food crust</td>
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<td>4710-4240</td>
<td>-27.04 (EA)</td>
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<td>5000-4730</td>
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<tr>
<td>11484</td>
<td>Food crust</td>
<td>5830±180</td>
<td>5210-4340</td>
<td>-27.46 (EA)</td>
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<tr>
<td>11842</td>
<td>Fishbone</td>
<td>7640±65</td>
<td>6630-6400</td>
<td>-26.78 (DI)</td>
<td>1.88</td>
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<tr>
<td>11844</td>
<td>Fishbone</td>
<td>7620±110</td>
<td>6680-6240</td>
<td>-26.78 (DI)</td>
<td>1.88</td>
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</table>
Table 4: Examples for hunter-gatherer pottery in Northern Europe. Some authors define the beginning of the Neolithic as the beginning of pottery production, not as the beginning of agriculture. The cultures characterised as “Neolithic” in this table were also hunter-gatherer cultures. Where only $^{14}$C ages BP were given, I calibrated them with OxCal 4.1, using the calibration curve IntCal09, and put the 95.4% age ranges in brackets (see text for references). This table shows that pottery similar to Ertebølle pottery was quite common for hunter-gatherers of Northern Europe. The datings in this table are not corrected for possible reservoir effects. The earliest appearance of Ertebølle-style pottery seems to be in the eastern Baltic (around 5000 BC), although the pottery from the Netherlands and Belgium also is quite old (from around 4700 BC). Pointed-based pottery seems to be a general phenomenon in Northern European hunter-gatherer groups, so that a single origin can not be identified.

<table>
<thead>
<tr>
<th>Site(s)/Region</th>
<th>Culture/Group</th>
<th>Age/Period</th>
<th>Description</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hüde I am Dümmer (NW Germany)</td>
<td>4200-3700bc (uncalibrated)</td>
<td>“large vessels with pointed bases, very similar to those of the Ertebølle/Ellerbek culture of the Baltic area”</td>
<td>Bogucki, P. 1988. <em>Forest farmers and stockherders</em>, Cambridge</td>
<td></td>
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<tr>
<td>Särnate (Latvia)</td>
<td>4045-2496 BC (my calibration; extremes of 94.5% ranges from 5 datings)</td>
<td>“conical vessels with straight or S-shaped rims and small ‘lamps’”</td>
<td>Dolukhanov and Liiva 1979 (see above)</td>
<td></td>
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<tr>
<td>Åland</td>
<td>Early Older Comb Ware Culture around 5000 BC; pottery from the same culture in Finland and Karelia, Russia: 5400-4200 BC</td>
<td>“un-profiled pots with a round or pointed bottom”, tempered with crushed rock, sometimes with sand, surface often decorated (cords, stamps)</td>
<td>Hallgren, F. 2004. ‘The introduction of ceramic technology around the Baltic Sea in the 6th millennium’, in Knutton, H. (ed.) <em>Proceedings of the Final Coast to Coast Conference 1-5 Oct. 2002 in Falköping, Sweden</em>. Uppsala, 123-142.</td>
<td></td>
</tr>
<tr>
<td>Eastern Baltic</td>
<td>Narva Culture</td>
<td>“…it should be safe to conclude that pottery appears</td>
<td>Hallgren 2004 (see above)</td>
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</table>
around 5500-5200 cal BC in the Narva Culture.”

Ertebølle clay lamps…”

“The richly decorated Ertebølle vessels display clear similarities to Narva pottery…”

<table>
<thead>
<tr>
<th>NE Poland, S Lithuania, SW Byelorussia</th>
<th>Neman Culture</th>
<th>Neman datings from Poland: 5900±100 BP, 5700±120 BP (5030-4529 BC, 4827-4335 BC) from Lithuania: 6550, 6020, 5980, 5950, 5360, all ±70 BP (the oldest: 5623-5374 BC)</th>
<th>vessels have slightly profiled shape and pointed bottoms</th>
<th>Hallgren 2004 (see above)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melsele-Hof ten Damme (NW Belgium)</td>
<td>Rhine-Meuse-Schelde-Culture</td>
<td>Mesolithic, although remains from domesticated cattle and pigs were found</td>
<td>“The potsherds are tempered with schamotte, bone and quartz and show pointed base vessels and sparse decoration”</td>
<td>Heinen, M. 2006. ‘The Rhine-Meuse-Schelde Culture in Western Europe. Distribution, Chronology and Development’, in Kind, C.-J. (ed.), After the Ice Age. Settlements, subsistence and social development on the Mesolithic of Central Europe. Stuttgart, 75-86.</td>
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<td>W Europe, Baltic</td>
<td>Mesolithic</td>
<td>pointed-based pottery is a characteristic trait of a range of subneolithic and mesolithic cultures along the whole of the Atlantic fringe and further to the east in the Baltic</td>
<td>Klassen, L. 2002. ‘The Ertebølle Culture and Neolithic Continental Europe: traces of contact and interaction’, in Fischer, A. and Kristiansen, K. The Neolithisation of Denmark. 150 years of debate. Sheffield, 305-317.</td>
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<td>Dabki 9, Baltic coast of Pommerania</td>
<td>6300-5300 BP (cal. 95.4% age range of 6800±500 BP: 6909-4621 BC)</td>
<td>“…Mesolithic flints, rich pottery collection of Ertebølle type with an admixture of Linear Ceramic pottery, […] and especially a growing number of bones from cattle and pigs.”</td>
<td>Kobusiewicz, M. 2006. ‘Paraneolithic - Obstinate Hunter-Gatherers of the Polish Plain’, in Kind, C.-J. (ed.), After the Ice Age. Settlements, subsistence and social development on the Mesolithic of Central Europe. Stuttgart, 181-188.</td>
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<td>Location</td>
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