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A Technique for Continuous Detection of Drill Liquid in Ice Cores

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Abstract

When drilling ice cores deeper than 100 meters, drill liquid is required to limit bore-hole deformation. Due to pressure differences in the ice, in Greenland typically between 800 to 1200 meters depth, the ice cores can crack during drilling. Ice from this "brittle zone" can be contaminated by drill liquid that seeps into cracks and this potentially contaminates chemical analysis of ice core samples. The Continuous Flow Analysis (CFA) system melts a subsection of the ice core, and analyses the ice for chemical impurities. Drill liquid can potentially interfere with the measurements or damage instruments. An optical detector was constructed to identify drill liquid in CFA tubing by UV absorption spectroscopy at a wavelength of 290 nm. To distinguish air bubbles from drill liquid, absorption was also monitored at 435 nm. The setup was successfully field tested in the frame of the NEEM ice core drilling project in Greenland. During 158 measuring runs, 27 proved positive for drill liquid. The instruments affected by drill liquid contamination were: the insoluble dust particle, the electrolytic conductivity, the ammonium, the hydrogen peroxide, and the sulfate detectors.

Danish resume

Når man borer iskerner dybere end 100 meter, er det nødvendigt, at bruge borevæske for at forhindre at hullet kollapser grundet isens flydning og tryk. Denne borevæske har samme densitet som isen, og har også nogle andre essentielle egenskaber som eksempelvis et frysepunkt meget lavere end den omkring liggende is.

Når sneen transformeres til is, fanges der luftbobler i isen. Disse luftbobler bliver komprimeret grundet vægten fra den ovenliggende sne og is. Et stykke nede i isen, ca 800 til 1200 meter på den Grønlandske indlandsis, er boblerne under sådan et stort tryk, at de begynder at blive mast ind i selve iskystal-strukturen. Efter 1200 meter er alle boblerne væk, men før det, er trykket så stort inden i isen, at når den tages op, så springer isen og slår revner. Borevæske trænger ind i disse revner, og når isen så senere bliver smeltet og analyseret med CFA apparatet (Continuous flow analysis), så kommer borevæsken ind i systemet. Dette giver fejlagtig data, da nogle af de forskellige detektorer reagerer med borevæsken.

Der blev bygget en optisk detektor, som kan detektere borevæske med UV lys på 290.00 nm. Desværre reagerer luftbobler på samme måde som borevæsken på denne bølgelængde, så 435.82 nm bliver ligeledes målt, da luftbobler her reagerer anderledes end borevæsken. Denne detektor blev efterprøvet i felten på NEEM, Grønland, 2011. Der blev lavet 158 CFA målinger af 1.1 m iskerne, og ved 27 af disse blev der målt tilfælde af borevæske. Følgende parameter i CFA reagerer med borevæsken og gav fejlagtige datapunkter: Uopløselige støv partikler, den elektriske lednings evne, ammoniakken, hydrogen peroxiden og sulfaten.

Ved hjælp af denne borevæske-detektor kan man identificere fejlagtig data. Her ud over vil en opstilling for at få borevæsken ud af systemet også blive præsenteret.

Preface

This thesis constitutes the concluding assignment of the author's Master degree in Geophysics. It is a 60 ECTS project and has had a time frame of one year.

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I had the unique opportunity to be a part of the NEEM ice core drilling project on the Greenland ice sheet. The experiences there, the camp members and in particular the CFA nightshift crew Gideon Gfeller and Aliza Benton, are some that I treasure beyond this work.

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Figure 0.0.1.: The NEEM CFA team: Hubertus Fischer, Gideon Gfeller, Olivia Maselli, Vasilios Gkinis, Aliza Benton, Kerstin Schmidt, and Me

Abbreviations

CIC	Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen
CFA	Continuous flow analysis
NEEM	North Greenland Eemian Ice Drilling (77°45N 051°09E, 2480m asl, www.neem.dk)
NGRIP	North Greenland Ice core Project
BP	Before Present
IPY	International Polar Year
ELA	Equilibrium-Line Altitude
ECM	Electrical Conductivity Measurements
IMER	IMmobilized Enzyme Reactor
Bern	Climate and Environmental Physics, Physics Institute, and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

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1. Introduction

In this day and age where climate, and its influence on humanity, is subject to so much debate, ice cores have become an important tool. Through analysing the ice cores we can gain insight into the past climate in a high annual resolution. In particular, the chemical composition of the atmosphere can be traced in the ice cores, and with this, we hope to understand the changing climate the earth is facing.

The state of the art, regarding chemical analysis of ice cores, is the Continuous Flow Analysis (CFA). The ice core is melted, and the melt water is analysed for impurities and chemical traces. The CFA system is fast, and measures with a high resolution using electric conductivity, fluorescence and absorption spectrometric methods.

The ice cores are drilled on the Greenland ice sheet and Antarctica, as well as several glaciers around the world. This paper is written at the Centre for Ice and Climate (CIC), Niels Bohr Institute, University of Copenhagen, and the CIC has for many years been the world leading centre for ice core drilling on the Greenland Ice Sheet.

When drilling for ice cores in deep ice, a liquid is pumped into the hole to prevent the hole from collapsing. The liquid must have the same density as the ice, have a low viscosity, and not freeze at the cold temperatures found in the ice sheet.

In early days, diesel fuel from airplanes was used. There was a lot of it in the field and it fulfilled the criteria, but it was not a very environmentally stable solution. The drill liquid composition has changed, as the demands for safety, environmental impact, and other properties introduced them self.

At the North Greenland Eemian Ice Drilling (NEEM) (77°45N 051°09E, 2480m asl, www.neem.dk), in 2010 and 2011 a drill liquid based on a coconut extract and an ester mixture was used.

At some point when drilling in the ice sheet, the drill reaches the brittle zone. A depth range in the ice where the trapped air is at a high enough pressure to shatter the ice when it is lifted up to the surface. When the ice shatters, drill liquid seeps into the cracks, contaminating the ice for the following chemical analysis.

In a recent article by [Svensson *et al.*, 2011] drill liquid contamination in the North Greenland Ice Core Project (NGRIP) [North Greenland Ice Core Project members, 2004] basal¹ ice cores, was the prime suspect in strongly elevated values in the dust measurements.

The goal of this work is to make a detector that can spot the drill liquid contamination. The detector needs to be able to detect NEEM drill liquid, but also NGRIP drill liquid as there is still much NGRIP ice left to analyse, that could be contaminated. A further goal was to have such a detector ready for the NEEM field season 2011. All these goals were achieved, and drill

¹The bottom part of the ice that slides on the bedrock

liquid contamination in the NEEM CFA data was identified and this information was used in the subsequent data analysis.

After the field season the goal is to find a way to remove the drill liquid, so that drilled ice cores can be analysed with out interference from the drill liquid. With the current knowledge the best viable solution and designed is presented in a later chapter, but it has yet to be built and implemented into the CFA system.

1.1. Empirical data

When this author first started looking into known publications about ice cores and the brittle zone, the general trend was much the same: The brittle zone is crap to work with! The ice cracks into little pieces and the scientist in the publications tend to skip that part of the ice as it was a lot of work for pure quality data. For those who wanted a completed ice core records the data contained in the brittle zone could be found in other drill sites, as the zone is depth dependant and not age dependant.

This thesis is primarily based on empirical data since no one has tried to continuously detect the drill liquid before, or given the brittle zone much interest. For the first time ever, at NEEM 2011, it was attempted to measure brittle ice with the CFA.

As there was not much literature on the subject of drill liquid contamination in the CFA system, and this author had extra time, a manuscript titled *A technique for continuous detection of drill liquid in ice cores* was drafted for the *Instruments and Methods* section in Journal of Glaciology. This manuscript can be found in the appendix, along with a Co-authorship statement. There were only forms for the PhD program, so this one is used.

This work was also presented at the International Polar Year (IPY) conference in 2012 in Montreal, in the form of a poster. It got a lot of positive response from the conference participants and even won 1st place in the *Area 1&2 - New frontiers, technologies and data practices in polar research* poster award.

The poster can also be found in the appendix.

1.2. Structure of the thesis

To understand the problem of drill liquid contamination in the continuous flow analysis system, the brittle ice and CFA system must be introduced before the development of the detector make sense. For this reason the rest of the thesis is structured like this:

Chapter 2 contains a description of ice sheet formation and development of the brittle zone.

Also the ice core drilling process and different kinds of drill liquid, their pros and cons, are discussed.

Chapter 3 describes the elements of the continual flow analysis system. Both the CFA system used in Copenhagen and the Swiss CFA system used at NEEM, and how they stand apart.

Chapter 4 is about how the drill liquid can be detected and the development of the drill liquid detector, along with observation of drill liquid behaviour in the CFA.

Chapter 5 is about field testing of the drill liquid detector at the NEEM ice core project. Both expected and unexpected drill liquid effects on the Swiss CFA are discussed.

Chapter 6 contains the method and analysis of the data collected at NEEM, described in Chapter 5.

Chapter 7 presents the results of the drill liquid detector. Where in the CFA analysis the contamination occurred and effects here of.

Chapter 8 describes the future prospects of this work. Finding a way to remove the drill liquid contamination before it affects sensitive systems.

Chapter 9 The Conclusion.

1.2.1. Project description of a experimental thesis project at CIC

Characterization and detection of ice core drilling fluids and their influence on chemical analyses of brittle ice.

Ice cores from Greenland contain an abundance of information about past climate over more than the last 100.000 years. Impurities in the ice/air matrix provide information about the environmental conditions in the past, such as emission sources, atmospheric long-range transport and deposition onto the ice sheet. At the Center for Ice and Climate (CIC) we have built a Continuous Flow Analysis (CFA) system for the study of major ions and physical constituents of ice cores, measured on a continuous stream of water produced from a heated melthead. The CFA system currently determines electrolytic melt water conductivity (a signal of ionic imbalance in the ice), sodium (deriving from sea salt), ammonium (related to biological processes and biomass burning events), sulphate (originating from volcanic eruptions and biological activity) and insoluble dust (transported principally from desert regions in central Asia).

Drilling fluids are required to drill ice below a depth of a few hundred meters in order to ensure that the drill hole does not collapse. The fluid must have a few essential properties - it must have a freezing point much lower than that of ice, it must have a density identical to that of ice, and it must be reasonably viscous. Ideally it should also be environmentally non-hazardous and safe to humans. Hydrocarbons are normally used to satisfy these conditions. For the NEEM ice core in Greenland, a combination of Estisol 240 (Coconut oil extract) and Coasol (ester mixture) has been applied. Ice cores are coated in drilling fluid when they are extracted, but when core quality is good, the drilling fluid does not contact the interior of the core which is used for chemical analysis by CFA. Brittle ice occurs in glaciers due to the compression of air bubbles with depth - the increasing pressurization of the air bubbles can shatter the ice core during drilling and extraction. In the case of brittle ice, drilling fluid can be introduced through breaks and cracks in the structure of the ice, and travel into the center where it may then disturb chemical measurements. Therefore a method to detect drill liquid is desired.

The aims of this project are:

- To characterize the optical properties of ice core drilling fluids such that they can be detected by optical means (absorption, transmission, fluorescence spectroscopy).
- To operate a spectrophotometer in the process of characterizing ice core drilling fluids
- To operate the CIC-CFA system for routine analysis of ice core samples
- To devise a method for identifying ice core drilling fluid in a stream of melt water, and implement this method in the CIC-CFA system. If possible, methods for the removal of drill fluid from the melt water should be explored.
- To apply these methods under field conditions at the NEEM ice core drilling camp, to determine chemical parameter(s) in ice contaminated by drill-fluid.

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2. Drilling Greenland Ice Cores

Greenland has many ice core drill sites, the first one was the Camp Century, 1962-66, where they drilled 1390 m down into the ice sheet [Dansgaard *et al.*, 1969]. More would later follow like Dye-3, 1979-80, 2037 m [Gundestrup and Hansen, 1984], GRIP 1989-92, 3029 m [Johnsen *et al.*, 1995], GISP2 1988-1993 3053.44 m, [Mayewski and Meeker, 1997], NGRIP 1996-2004, 3085 m [North Greenland Ice Core Project members, 2004], and recently NEEM [Larsen *et al.*, 2012; 2011] from 2007 to 2012, where they drilled 2542 m down to the bedrock. These are just a few of the many ice core drilling's around the world on glaciers, Antarctic, and other parts of Greenland.



Figure 2.0.1.: A map showing the location of the ice core drilling sites NEEM and NorthGRIP along with previous drill sites on Greenland.

2.1. What knowledge is hidden in the ice?

The climate diary of the northern hemisphere can be read in the Greenland ice sheet. Each year a new layer of snow falls that turns into an ice layer. By drilling down into the ice and retriev-

ing the ice cores we can through various analytical methods read this climate diary, layer by layer.

The founding father of the Centre for Ice and Climate, Willi Dansgaard, discovered that the concentration of heavier oxygen isotopes changed during a passage of a rain front [Dansgaard, 2004]. This sparked the research into Oxygen isotopes, $\delta^{18}\text{O}$ and Deuterium δD , that are proxies for the temperature at the precipitation location and source area for the precipitation [Masson-Delmotte et al., 2005]. Figure (2.1.1) shows the preliminary $\delta^{18}\text{O}$ data from NEEM. At higher temperatures the atmosphere contains more moisture and there by a higher concentration of the heavier oxygen isotopes (-35 to -30). At colder temperatures the precipitation contains a lower concentration of $\delta^{18}\text{O}$ (-35 to -46), as depicted in the figure. This is the last ice age. The $\delta^{18}\text{O}$ in the precipitation is dependent on the temperature, but also the elevation of the ice sheet, and with this the height of the past ice sheet can be estimated [Vinther et al., 2009]. When looking at ice core data, the $\delta^{18}\text{O}$ plot seems to be the norm with in the ice core community. This is why the brittle zone is marked in grey on a $\delta^{18}\text{O}$ plot. All the ice measured in this thesis comes from this area, placing it in the late Holocene about 4-10.000 yr before present.

Air bubbles caught in the ice, contain samples of the past atmosphere. The chemical composition of the old atmosphere and amount of greenhouse gasses can be measured in these bubbles [Schwander and Barnola, 1993].

The impurities in the ice, also describes the composition of the atmosphere in the past, as well as local and global conditions. An example would be a very dry climate will put a lot of dust into the atmosphere, that in turn, will land on the ice sheet [Jickells et al., 2005].

Cosmogenic isotopes are created in the upper atmosphere due to cosmic radiation. The amount produced is related to the strength of the earth's magnetic field. Carbon-14 (^{14}C) is probably the best known isotope, as it is used for radiometric dating. On the ice sheets the relation between Beryllium-10 (^{10}Be) and Chlorine-36 (^{36}Cl) is more suited for radiometric dating of the ice, as the amount of ^{14}C is very low here. [Beer et al., 2002]

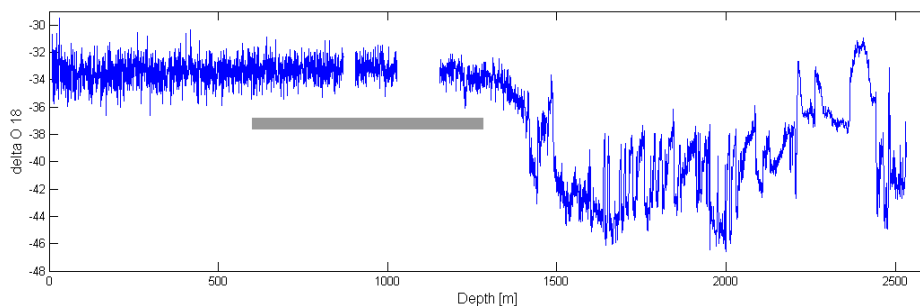


Figure 2.1.1.: The preliminary $\delta^{18}\text{O}$ result from NEEM. As $\delta^{18}\text{O}$ is a proxy for past temperatures. The present high values (at low depth) is the interglacial period, and the lower values at depth 1500 m and below is the last glacial period. The grey bar indicates the brittle zone, that is the focus of this thesis.

2.2. Ice formation

To understand what brittle ice is, one first needs to understand the process of the snow to ice transformation. The transition from snow to ice involves, the snowflake breaking down in to smaller bits, some evaporate and others gain mass and through this densification a formation of porous channels occur. Through these channels, an exchange of gasses between the snow pack and the atmosphere happens. Later these pores close and the gases are trapped in the ice. The following is the process step-by-step.

1. When the snow falls on the ice sheet it makes a light, low density layer, with lots of air and only fine ice crystals that are the snow flakes.
2. The strong wind compacts this new snow layer, along with grinding, the snow flakes are broken. The snow layer is now of a higher density, but still with a lot of air in these ice splinters.
3. More and more layers of snow will accumulate on top of this layer, applying pressure, and thereby compacting the snow layer even more. But still there is a lot of air, that has contact to the atmosphere. See the first 0-15 m of Figure (2.2.1)
4. Due to the pressure a process called *pressure-sintering* takes place [Paterson, 1994]. The ice crystals exchange mass, change shape and size due to sublimation. This transition between snow flakes and solid ice is called *firn* and it consist of small ice grains frozen together. The air diffuses slowly through the firn. See Figure (2.2.1 depth 15-50m)
5. The sintering and sublimation continues, the density rises, and at some point, there is *pore close off*. The air pockets, pores, are now isolated and no longer connected to the atmosphere. The depth of the close off depends on the accumulation. In high accumulation areas (0.5m/yr) the age difference between the air and the surrounding ice can be a few hundred years. If the deposition is slow (0.05/yr) the age offset can be as large as 2000 years. [Ruddiman, 2001]
6. The hydrostatic pressure from the ice, compacts the air bubbles, and the air pressure increases.
7. At a particular depth, this differs from ice sheet to ice sheet, below 1100 meters at Byrd station, Antarctic [Paterson, 1994], below 1200 meters at NEEM, Greenland, the bubbles disappear. The air is squished out into the ice matrix, so it is still there in the form of *clathrate hydrate* see Figure (2.2.2).
8. The ice is now solid bubble free ice.
9. At the bottom there can be melt due to pressure, geothermal heat flux, and turbulence due to bedrock topography. As the warm ice is brought up through the colder ice it can become brittle as the liquid water between the ice crystals freeze [Svensson et al., 2011].

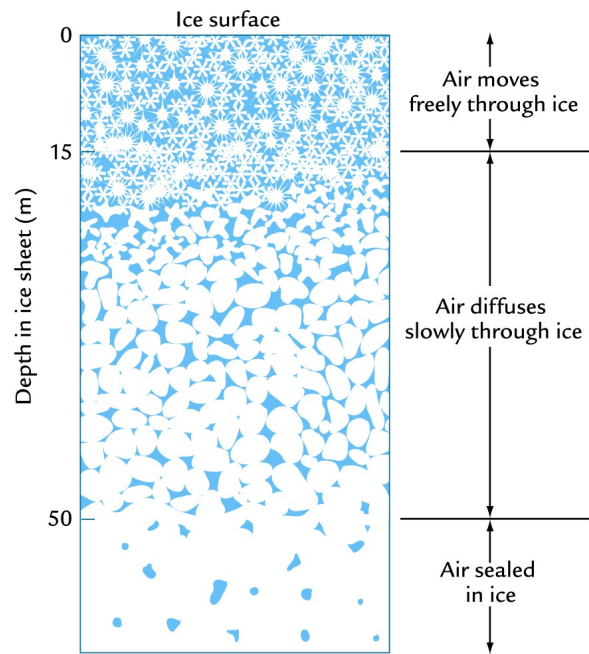


Figure 2.2.1: The light fluffy snowflake at the surface, gets compacted into ice grains. The air pores still have contact to the atmosphere. Deeper the pores close off, sealing the air in the ice. The depth of the close-off varies according to accumulation. Figure by [Ruddiman, 2001]

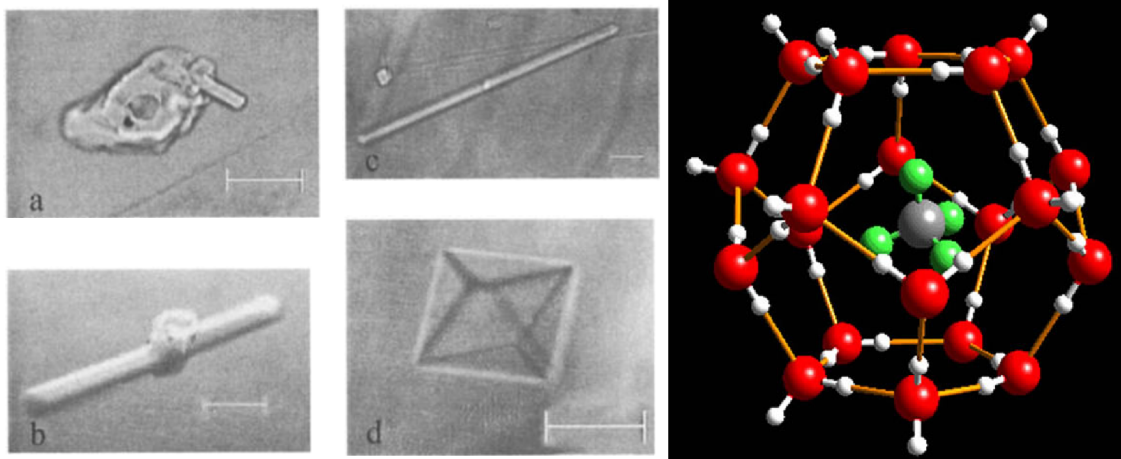


Figure 2.2.2.: Observed clathrates in the ice, where there air from the bubbles has been squished into the ice matrix, as seen on the right. Taken from depths of 1272 m (a), 1204 m (b) and 1272 m (c/d) [Kipfstuhl et al., 2001]. Scale bar is 100 μm .

On the right a methane atom caught in a clathrate.

2.3. Brittle zone

The transition area where the air bubbles are squished into clathrate hydrate is known as the brittle zone (e.g 500-1200 m for Vostok, 900-1600 m for GRIP [Kipfstuhl *et al.*, 2001] and, 601-1281m for NEEM [Larsen *et al.*, 2011]). The air bubbles are at 50-100 times surface atmospheric pressure. When this ice is drilled and transported up to the surface, the ice moves from an area with $\approx -35^\circ\text{C}$ or lower, to $\approx -20^\circ\text{C}$, and the pressure goes from ≈ 100 to below 1 atmospheric pressure¹. These changes to the ice introduce so much stress, that the ice cracks and shatters as it is retrieved from the drill.

The brittle ice core is given time to relax, in which the ice core volume expands up to 0.6% [Gow *et al.*, 1997], due to micro fractures, bubble depressurisation, and healing of major fractures. This leads to a reduction in the brittleness of the ice, permitting cores to be cut on a band saw with out the same amount of shattering that occurs with freshly drilled brittle ice. The NEEM 2011 brittle ice, drilled in 2009, was analysed after a resting period of two years, to relieve the internal stresses, and even then, the ice was very fragile.

2.3.1. Ice flow

The ice sheet is a dynamic body of flowing ice. Snow deposited on the top part of the ice sheet, above the Equilibrium-Line Altitude (ELA), survives the summer melt. With the next years precipitation, the snow pack accumulates, compacts into firn and then ice. The compressed and displaced ice flows slowly towards the ice margins. At the margin, the ice is removed by melting or by discharge of icebergs into the ocean. In Figure (2.3.1) thicker annual layers flow slowly vertically and faster horizontally, thinning the annual layers. Due to these different flow velocities the annual layers will displace. At some outlets the annual layers have been turned up to 90 degrees and you can walk across several annual layers.[Schaefer *et al.*, 2009; Petrenko *et al.*, 2006]

It is only at the ice divide where the horizontal velocity field is close to zero, that the layers are neatly stacked on top of each other. The oldest ice layers are found near ice divides.

At the drill site the ice must also be thick, as large ice thickness implies more visible/detectable annual layers. The bedrock must be flat, because uneven bedrock causes irregular ice flow that can disturb the ice layers. The precipitation should be moderately high at the drill site. With a high annual snowfall the ice flow speeds up, thinning the lower older ice layers, making them harder to detect. A low snowfall will result in thin annual layers that are harder to detect and analyse. With a moderately high precipitation the layers are thick enough to detect, but the ice flow is low enough, so the bottom layers do not thin beyond measure.

¹NEEM camp is $\approx 2.5\text{km}$ above sea level, so the atmospheric pressure is lower than normal surface pressure.

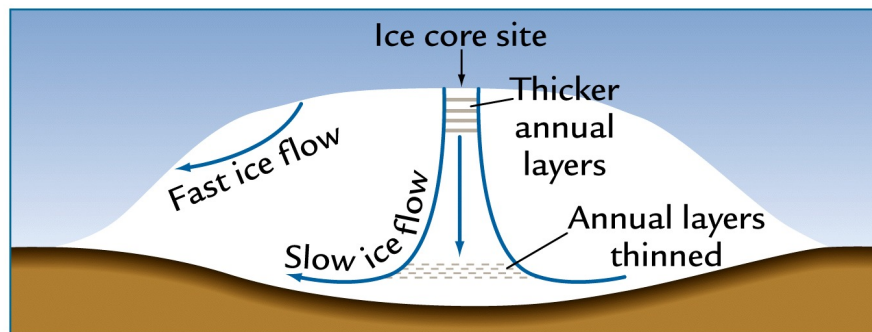


Figure 2.3.1.: As ice accumulates, the annual layers thins and extends towards the ice margins. Figure by [Ruddiman, 2001]

2.4. The drilling process

There are tree kinds of drills used by the Danish Centre for Ice and Climate.

The "hand auger" is a simple and light drill system. With connection rods it can extend down to 10 m depth, and it retrieves 74 mm diameter firn cores. This drill consists of a drill head with ice cutters made for firn drilling. The core barrel holds the core when it is pulled to the surface.

When rotated by hand, the drill head with the standard 3 cutter configuration, cuts into the firn, while the barrel fills with the untouched firn core. The auger on the outside of the barrel drives the ice shavings up along the side. When the core is removed at the surface, the drill is lowered back into the borehole and the process is repeated. Meanwhile the firn core is fitted together, measured, labelled, and packed into ice core boxes ready to be shipped back for analysis [CIC Webpage, 2012].

The "shallow drill" is much larger and much more complex. At about 800kg the shallow drill is 10 times the weight of the hand auger. It is electric, like the deep drill (described later), and works in much the same way, but it is smaller, lighter and therefore transportable. Like the hand auger it retrieves 74 mm cores from a depth of up to 350 m [CIC Webpage, 2012].



Figure 2.3.2.: The hand auger with a shallow ice core, picture by Antje Fitzner, NEEM 2011

The "Hans Tausen" drill (HT drill) [Johnsen *et al.*, 2007], is larger than the shallow drill, and is used for deep drilling. It is an electro-mechanical drill used to retrieve 1.7 m long 98 mm diameter cores from 2 m below the surface down to bedrock [CIC Webpage, 2012]. The "deep drill" is a modified version of the HT drill used at NGRIP. The core barrel has been extended to hold up to a 4 m ice core. The drill had another necessary modification as the new NEEM drill liquid has a higher viscosity than the NGRIP drill liquid.

From 2 m below the surface down to ≈ 150 m the drilling is dry. This is firm and the first 50-70 m of the ice core. During this part of the drilling there is no need for drill liquid. For one the firm is so porous that any drill liquid would seep out, but also the borehole can maintain its shape on its own. 150 m down to ≈ 450 m is done in wet drilling mode, and drill liquid is used. Without the drill liquid the sudden release of stresses in the ice causes the ice core to crack, and the internal fractures reduce the ice core quality significantly. Drill liquid prevent this when it is added to the borehole, and the stresses are reduced, keeping the core quality high. Below ≈ 400 m, the drill liquid serves another purpose: To keep the pressure in the hole approximately the same as in the surrounding ice. Otherwise the ice would deform due to the ice flow and pressure difference, and close the hole, risking getting the drill stuck deep in the ice. In that case *ethylene glycol* can be used to dissolve some of the ice and get the drills free again [Johnsen *et al.*, 2007]. More about the different kinds of drill liquid used in different projects, later in section 2.5

Figure (2.4.2) is a schematic of the deep drill. The drill head cuts away a ring of ice ≈ 2 cm wide with an inner diameter of 98 mm. The ice core slides into the inner core barrel (with the spirals), while the chips move up between the inner core barrel and the outer barrel. The brass section is the pump, which pumps drill liquid with chips into the chips chamber, where the chips are retained before the drilling liquid is recycled through the hollow shaft. In reality, both the inner core barrel and the chip chamber are about 4 meters long, but they have been shortened here for clarity.

The middle section of the drill contains a pressurised compartment including the motor and

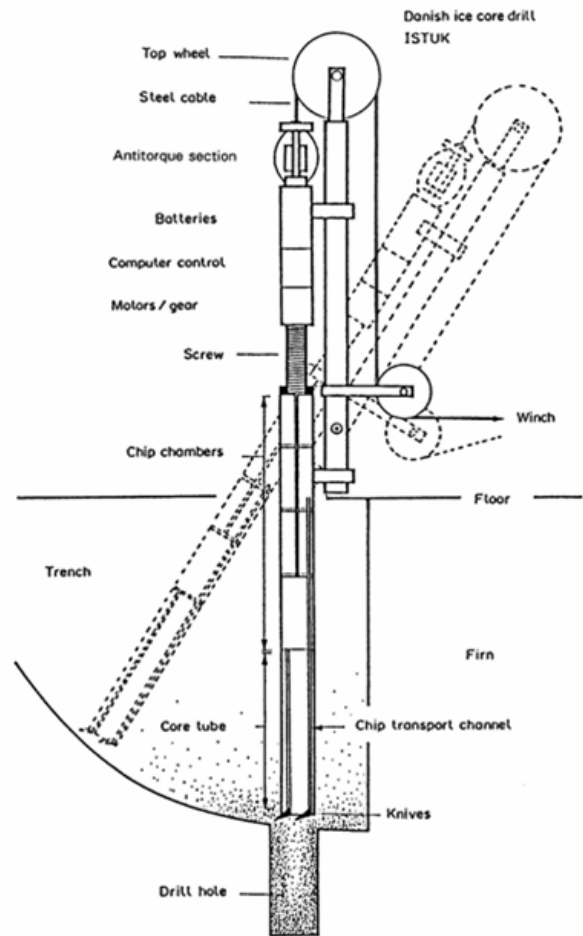


Figure 2.4.1.: The drill tower pivots. This enables the operators to remove the ice core or do maintenance horizontally and then send the drill vertically back into the ice.

electronics section. Near the base of the ice sheet, the pressure is about 270 times the atmospheric pressure at sea level, so the seals must be of very high quality.

The top part of the drill is the anti-torque section that prevents the drill from rotating in the hole. Three spring-loaded blades cut their way into the ice and ensure that the motor rotation makes the drill head and pump rotate, instead of spinning the entire drill the opposite way.

The drill contains up to 4 m of ice core. After a section has been drilled, rotation is stopped, and the cable is pulled. Small spring-loaded knives - "core-catchers" - cut into the ice core and prevent it from gliding out of the drill. A force corresponding to a drag of 400-1000 kg is needed to break the ice core, which is then brought to surface.

On the surface, the drill ends on the pivoting tower, Figure (2.4.1), where in a horizontal position the drill is disassembled, and the core is pushed backwards out of the inner core barrel. The chips are removed, and after re-assembly, the drill is ready for another trip to the interior of the ice cap.

Drilling through the ≈ 2.5 km of ice at NEEM requires 8-900 drill runs, each taking from 40 minutes to several hours depending on the depth. The drilling started in 2008, and was completed late in the 2010 field season. [NEEM Webpage, 2012]

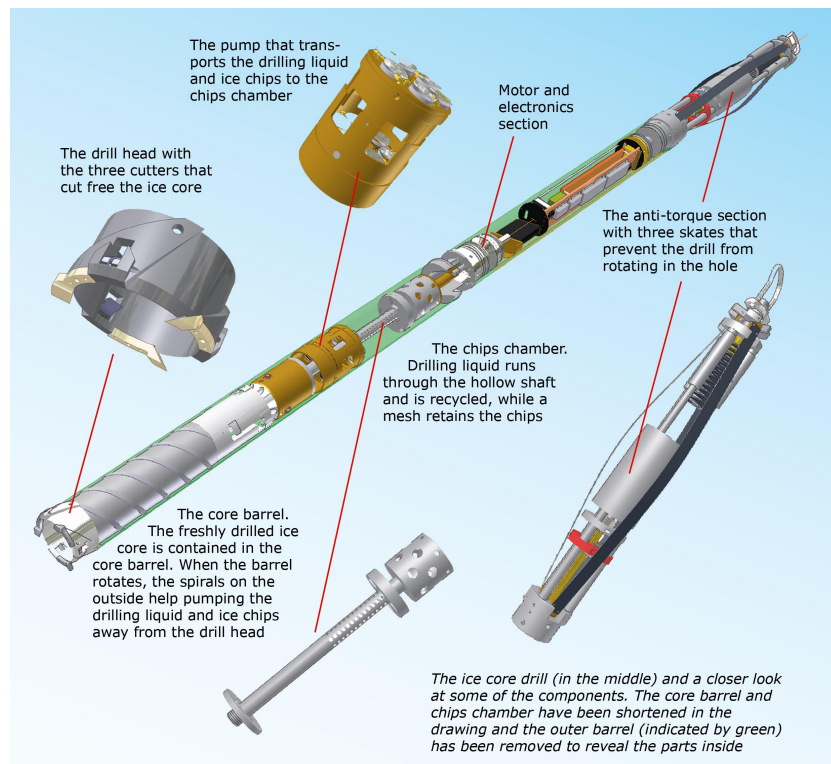


Figure 2.4.2.: The Hans Tausen drill is about 13.5 meters long, and is shown here with the outer barrel (indicated by green) removed. When operational, only the drill head and the anti-torque section (lower right) are visible.

2.5. Drill liquid properties

The first ice core drilling with drill liquid was done at Camp Century in 1966. The lower part of the borehole was filled with aqueous ethylene glycol solution and the upper part was filled with a mixture of diesel fuel and a densifier (trichlor-ethylene) [Talalay and Gundestrup, 2002]. The choice of drill liquid is treated as one of the most important parts of drilling technology, as ice core quality and the drills safe retrieval depends on it.

Density and fluid level The drill liquid provides hydrostatic compensation from the lithostatic² pressure of the surrounding ice. If the fluid level is too low, the borehole closes, and the drill gets stuck.

Viscosity The time of lowering and hoisting takes from 50 to 90 % of the total drilling time. This affects the total ice core production per day, and thereby the cost of the entire drilling project. Therefore a low viscosity is wanted that allows a faster travel time for the drill.

Frost-resistance The drill liquid should not freeze during storage or in the bore-hole. This parameter is particularly important in central Antarctica (as for example, the average annual temperature at Vostok station is -57°C and absolute minimums are -89.2°C)

Stability It is important that the drill liquid does not change properties during storage, transportation or in the borehole. Some kinds of hydrocarbons containing petroleum products react with oxygen and metals. [Talalay and Gundestrup, 2002]

Compatibility with polymers and metals The drill liquid should be non-aggressive to the drill and electronic components. This author observed how the estisol in the NEEM drill liquid made the rubber swell and become elastic on an iPod cable. However, a wide variety of seals and gaskets are not affected.

Volatility and flammability The volatility problem is a delicate one. On the one hand high volatility raises health and fire safety questions. With a high rate of vaporisation, air contamination needs careful control, and with that in mind, a low rate of vaporisation is preferable. On the other hand, the benefit of high volatility is a clean workspace. Clothes become clean after a short time, the floor is not slippery and the ice core is easy to handle.

Ice and water solubility This is the Hydrophilic³ vs. Hydrophobic⁴ discussion. Hydrophilic solutions like ethanol + water [Zagorodnov *et al.*, 1994] can have the appropriate density, low flammability, generally low toxicity, relatively low cost, low environmental hazard potential and other desirable characteristics. The problem is the reaction to the ice itself. It continuously dissolves the borehole walls, the core, and chips until slush forms. The presence of slush alters the density of the hydrophilic solution, resulting in an unstable bore hole and/or stuck drill. Increasing the amount of ethanol should prolong the lifetime of the borehole [Zagorodnov *et al.*, 1994; Gerasimoff, 2003].

Hydrophobic liquids like oil hydrocarbons, like *Exxol D40*, are insoluble in water and completely inert to the ice at negative temperatures. The ice does not lose weight during

²Overburden pressure from the surrounding material (ice)

³Water loving

⁴Water fearing/repelling

several days in contact with hydrophobic liquid [Talalay and Gundestrup, 2002], but these often need a densifier, like *HCFC 141b* (more in section 2.6). One of the few compounds that has suitable density of its own, is *n-butyl acetate* and *Estisol 140* that was tested at NEEM 2012 as another one-compound-drill-liquid (See table 2.1 for more details on Esitsol 140).

Toxicity The drillings sites may be outside the normal national boundaries, but the health and safety of drillers, scientists, technicians and support personnel is still very important. The toxicity levels may vary from country to country, and different restrictions at the drill site are enforced. An example from the past; After working a workday in the drilling shelter, drillers that used *n-butyl acetate* reported dizziness and headaches [Zagorodnov *et al.*, 1994].

Environmental characteristics After a drilling campaign has been concluded, the borehole is closed and left with the drill liquid inside. It is almost impossible to retrieve the drill liquid. Many of the previously mentioned and proven densifiers have been considered too toxic, or are no longer available due to the Montreal Protocol⁵ on ozone-depleting substances. *n-Butyl acetate* has quite good biodegrading properties and evaporates fairly quickly. Ethanol is easily biodegradable, natural and a widely occurring product [Zagorodnov *et al.*, 1994].

Transportable From a logistic point of view, the drill liquid must be transportable in air planes, as this is the main access to the drilling sites.

Cost The purchase and delivery of the drill liquid can be a significant point in the drilling projects budget. A simple calculation: A hole of 0.13 m diameter and 2542 m high, gives a column of drill liquid about 33.72 m³. According to the NEEM field leader there was ordered about 40 m³ of fluid for the entire NEEM drill project. A total of 960.000 DKK.

2.6. NGRIP Drilling Liquid Properties

At the North Greenland NGRIP site Exxsol D-series solvents, D-40, were used with hydrochlorofluorocarbon 141b (HCFC-141b) as a densifier [Murshed *et al.*, 2007].

Some concern was raised about the NGRIP drill liquid. It was observed that the HCFC-141b densifier reacted with the sub glacial water forming hydrates⁶. These hydrates could block the borehole. It was also claimed that the densifier would, to a limited extent, bond with the ice shavings from the drilling process and thereby increasing their density [Murshed *et al.*, 2007]. From an environmental point of view the HCFC-141b is still a hazard to the ozone layer.

⁵The Montreal Protocol (1987) on Substances that Deplete the Ozone Layer (a protocol to the Vienna Convention for the Protection of the Ozone Layer) is an international treaty designed to protect the ozone layer. http://en.wikipedia.org/wiki/Montreal_Protocol

⁶Hydrate is a term used in chemistry to indicate that a substance contains water. <http://en.wikipedia.org/wiki/Hydrate>

2.7. NEEM Drilling Liquid Properties

During the NEEM drilling, a new drilling liquid has been developed for NEEM, based on Estisol 240 (coconut oil extract) mixed with Coasol (ester mixture). This liquid is non-polar⁷, non-hazardous, has no explosive risk, a low environmental impact, and is freely available. It is twice the price of the NGRIP drill liquid D-40/HCF-141b and has 5 times the viscosity at -30°C. See Table (2.1) for details on the Estisol and Coasol.

An apparent fault with this drill liquid is that it is not suitable for borehole temperature logging, in particular the bottom 100 m. There is a lot of temperature advection in the warm bottom part of the ice. In the bottom 100 m the advection interferes, the rest of the borehole is not affected.

Estisol 240 was field tested as a drilling liquid at *Flade Isblink*, Greenland 2006 with a the Hans Tausen electro-mechanical drill [Johnsen *et al.*, 2007]. The drill and drill liquid produced ice cores at a "good" quality, with no problems cleaning and processing the ice, even though the drill liquid is very slippery.

The mix proportions for NEEM fluid, 2 parts Estisol to 1 part Coasol.

Table 2.1.: The properties of the drill liquid [Larsen *et al.*, 2011; 2012].

Table	Coasol	Estisol 240	Estisol 140
Manufacturer	DOW	DOW	DOW
Melting point	< -60 °C	< -50 °C	< -89 °C
Boiling point	274 - 289 °C	255 - 290 °C	199 °C
Flash point	131 °C	136 °C	75 °C
Explosive limit	0.6 - 4.7 % (vol)	None	None
Vapour pressure (2 °C)	0.004 kPa		
Density (20 °C)	960 kg/m ³	863 kg/m ³	865 kg/m ³
Density (-30 °C)	995 kg/m ³	898 kg/m ³	915 kg/m ³
Viscosity (20 °C)	5.3 cSt	3 cSt	1.0 cSt
Viscosity (-30 °C)	25 cSt	13 cSt	2.2 cSt
Auto ignition temperature	400°C	None	270°
Bio-degradable	Yes	Yes	Yes
Fire fighting equipment	Water spray, foam, CO ²	Water spray, CO ² , foam, dry chemical	Water spray, CO ² , foam, dry chemical
Special protection	No	No	No
Hazardous material	No	No	NO
Explosive risk	None	None	None
Max. Workplace air levels	None	None	None
Price US\$ equiv. in Kg	5.50 \$ /Kg	4.60 \$ /Kg	4.5 \$ /Kg

⁷Will not react with water

2.8. Ice core processing

When the ice core is retrieved from the drill at NEEM, it is documented, placed in an aluminium holder and carried from the Drilling Trench into Science Trench and placed in the buffer areas shelf. From here the ice core is measured, cut and bagged. Some measurements are done in the field, while others are done in the respective labs around the world. The brittle ice is kept in storage for two years before it is processed. This is to reduce the tension inside the ice and give the drill liquid time to evaporate.

A few analytic methods are non destructive to the ice. The Electrical Conductivity Measurements (ECM) measures the conductivity of the ice, identifying volcanic layers as the sulphuric acid is conductive. This gives an indication of the time the ice belongs to, as previous volcanic eruptions have been dated and identified. After the first cut in a horizontal saw, the Phys.Prop, see Figure (2.8.1), the core will be mounted in the Danish ECM setup for DC conductivity measurements. Afterwards, the core will be returned to the horizontal saw for cutting the central slab, the SC+CFA+ISO, see Figure (2.8.1).

The 36 mm thick central slab will be polished on both sides with a microtome knife and then scanned in the line scanner see Figure (2.8.2). The camera records the light reflected from the dust and impurities in the ice. In this way the layer is visible, the *visual stratigraphy*, and disturbance of the individual layers can be identified.

Some Continuous Flow Analysis (more in section 3) measurements were conducted in the field to reduce contamination of the ice cores, but otherwise the ice core was cut according to Figure (2.8.1), bagged, and packed into ice core boxes for later transport.

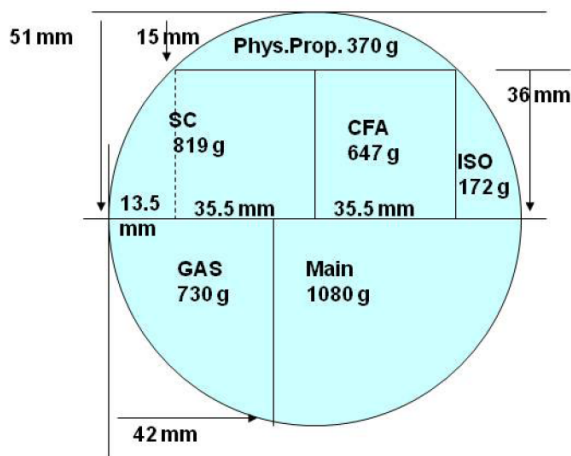


Figure 2.8.1: Schematic of the core cut, the CFA piece has no connection to the core surface and is therefore an uncontaminated part of the ice.

Phys.Prop Physical properties covers ice crystal structure, size and direction.

CFA The piece used in Continuous Flow Analysis, this will be covered in the following chapters.

ISO The stable isotopes $\delta^{18}\text{O}$ and δD . Temperature proxies for the site and source area.

GAS This piece of ice is used for gas analysis, in particular gasses that do not react well to be melted out of the ice.

Main The main core is saved for future references. Researchers can apply for sample pieces of the main core.

SC The Steering Committee piece. A secondary Main core or CFA piece.

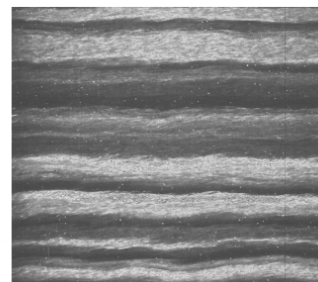
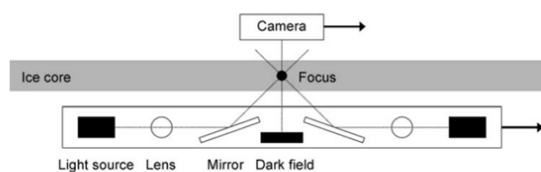


Figure 2.8.2.: The central slab of the ice is cleaned with a microtome knife and then scanned in the line scanner. The dust and impurities in the ice scatters the light reflecting it to the camera. The result is the visual stratigraphy, the layers of white impurities and the clean black ice.

3. Continuous Flow Analysis

In 1969 Clair C. Patterson needed a 2 foot (≈ 61 cm) square cube of snow/firn to get one lead (Pb) data point [Cohen, 1995]. Now we need a the $35\text{ mm} \times 35\text{ mm} \times 1\text{ mm}$ or less to get 1 data point from several components. The Continuous Flow Analysis (CFA) system, melts the section of the ice core as seen in Figure (2.8.1), and the stream of melt water is then analysed for trace chemicals. The measurements are continuous and with a high resolution. With this data we can get an insight into past climate events and count the annual layers after other methods have given up. The CFA is a complex system of very narrow water lines, transporting the melted ice water to detectors, mixing it with reagents along the way.

3.1. Preparation of the ice

After the ice core has been drilled, and is ready for processing, the ice is cut into different segments. Since the CFA is very sensitive to contamination, the ice is cut from the center of the core with no contact to the core surface, see Figure (2.8.1). The stick of ice is $35.5\text{ mm} \times 35.5\text{ mm} \times \text{Core length}$. Due to the dimensions of the ice core boxes in the early Greenland drilling days, an ice core is 55 cm long. The top and bottom of the ice stick is cut perpendicular to the length and cleaned with a microtome blade. The stick of ice is then placed in a plexiglass container that fits vertically on top of the melt head. See Figure (3.2.1 & 3.2.2)

A small piece of ice made from ultra clean Milli-Q water (Milli-Q, $\geq 18.2\text{M}\Omega/\text{cm}$, Millipore Advantage) is likewise cut and cleaned, and placed at the very beginning of the ice core and is the first to be melted when the measurements start. This Milli-Q ice cube serves several functions: It will fill the lines from the melt head to the pumps with Milli-Q water, while the CFA is running idle, and it will give the CFA operators time to stop and reset in case of system failure, with out loss of valuable ice core.

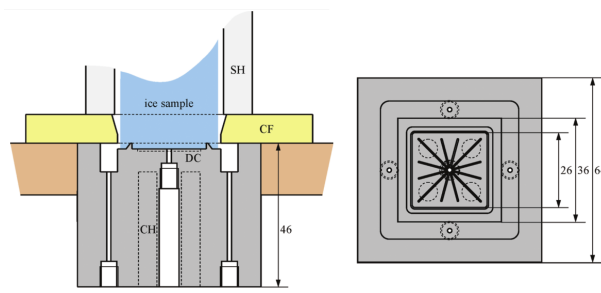
3.2. Melting

After the ice has been prepared, it is placed vertically on the melt head, see Figure (3.2.1), that melts the ice from the bottom. The melt heads used in the Copenhagen CFA, are usually made of aluminium, with high thermal conductivity, and the surface is coated with PTFE¹. The melt head is designed with a wall, so the melt water from the outside of the ice is channelled into the outer sample, while the inner core of the ice is channelled into the inner sample. This inner sample from the middle of the ice is free from contaminants and this is used for the analysis. The outer sample is considered contaminated due to handling and all the outer sampling is going to the wast bucket.

The melt head is heated to $15\text{C}^\circ - 35\text{C}^\circ$ depending on the desired melting speed. The ice is

¹A hydrophobic type of Teflon. <http://en.wikipedia.org/wiki/Polytetrafluoroethylene>

Figure 3.2.1: Melt head with drain channels (DC) and holes, cartridge heaters (CH), centreing frame (CF), and removable rectangular plexiglass sample holder (SH), measures are in mm [Bigler *et al.*, 2011].



pressed against the melt head by its own weight, plus a weight made of steel of $\approx 100g$. This ensures a constant melt speed, especially at the end of the melt where the weight of the ice it self is going towards 0g. Attached to this weight is a wire that leads down to an encoder that measures the melt speed. Copenhagen CFA has a melt speed of ≈ 9 mL/min meltwater including 10% air. In order to prevent contamination, an overflow from the inner to the outer melt head area of $>10\%$ is created by pumping only ≈ 8 mL/min sample to the analysis system [Bigler *et al.*, 2011].

The inner melt water sample, now only referred to as sample, is pumped through the system by a peristaltic pump². The sample goes through a debubbler, where the air trapped in the ice, $\approx 10\%$, is removed from the sample. This makes a steady flow without the bubbles that otherwise interfere with some of the instruments. The removed air can be analysed for trace-gasses like Methane at an adjoining lab, but is not in it self, a part of the CFA system. From the debubbler the sample is split into different lines, leading into different detectors and measuring devices. The measurement of dust and conductivity are noninvasive and are on the same line, while measurement of chemicals like Ammonium and Sulfate, need separate lines for adding the appropriate buffer and reagent for the absorption or florescence detection method.

²A peristaltic pump, or roller pump, is a type of positive displacement pump. The fluid is contained within a flexible tube fitted inside a linear pump casing. A rotor with a number of "rollers", attached to the external circumference compresses the flexible tube. As the rotor turns, the part of tube under compression is pinched closed thus forcing the fluid to be moved through the tube. http://en.wikipedia.org/wiki/Peristaltic_pump

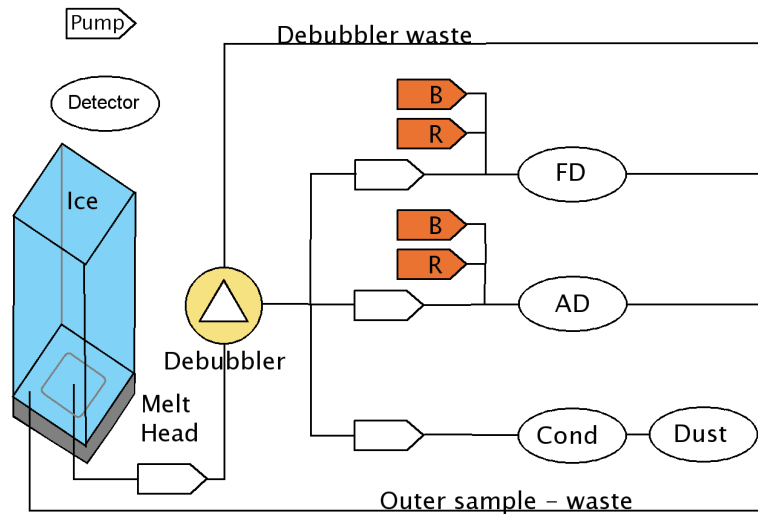


Figure 3.2.2.: A simplified schematic of the CFA setup.

The ice is melted and the centre part is pumped (arrow boxes) into a debubbler (orange circle with triangle) where air and water is separated. From there the sample stream is split and pumped to the different detector systems. A reagent (R) and buffer solution (B) is added to the sample before it reaches the fluorimetric detector (FD) or absorption detector (AD). For electrolytic conductivity (Cond) and insoluble dust particles (Dust) measurements, no reagents are needed.

3.3. How the CFA works

The CFA system primarily works by shining light through the sample water, the light will either be dimmed or it will glow. These methods are absorption and fluorimetric detection. The only components of the CFA that do not work in this way are the electrolytic conductivity of the melt water (hereafter conductivity) and insoluble dust particles (hereafter dust). In the Copenhagen CFA dust, conductivity, sodium and ammonium is measured, but other CFA systems around the world are configured in other ways. In particular the CFA from Bern, Switzerland, detects more components at the cost of resolution as described later on.

3.3.1. Absorption detection

This method works by introducing a reagent to the ice water sample, mixing it, adding a buffer to stabilise the mixture, and letting it pass through a light beam in a flow cell. See figure (3.3.1).

Beer-Lambert's law states that the amount of light absorbed over the distance l is related to concentration of the compound measured.

$$A = \epsilon lc = -\log \frac{I_1}{I_0} \quad (3.1)$$

where A is absorbance, ϵ is the wavelength-dependent molar absorptivity ($M^{-1}cm^{-1}$) (extinction coefficient), l is the cell length (cm) and c is the molar concentration of absorbing species. I_0 and I_1 is the light intensity going in and out of the cell.

There is a trade off with the cell length. A longer cell length produces a stronger signal to the cost of temporal resolution, and vice versa.

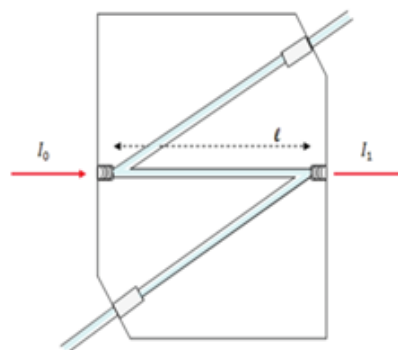


Figure 3.3.1: As the sample flows through the cell, light with intensity I_0 shines through and gets absorbed over the cell length l , allowing light to escape with intensity I_1 . This change in light intensity can be translated to concentration.

3.3.2. Fluorimetric detection

Although this method seems hard to grasp, the principle is known from every nightclub, as you pass under the blacklight the white t-shirt glows as the UV makes the bleach fluoresce.

The sample is mixed with reagent and buffer, and exposed to light at one wavelength, and it fluoresces at another. The intensity of this is converted into a molar concentration.

3.3.3. Conductivity

As the sample water flows past two electrodes in the conductivity flowcell (Amberscience 3082 with micro-flowcell), all the ions conduct current. The conductivity is a measurement of all the ions available. As Ca^{2+} (Calcium, soluble dust particles) is the most abundant ion the conductivity follows dust closely, but also volcanic signals are visible as the SO_2 Sulfate, emitted by the volcano will show up as H_2SO_4 .

3.3.4. Dust

The term mineral dust covers insoluble particles, that are measured with an (Klotz Abakus, Germany). The water sample enters the Abakus and is channelled through a very narrow split, where it is assumed only one particle can fit at the time. This aligns all the dust that passes through a laser beam, mounted orthogonal to the flow. As the particles enter the beam, the amount and size are registered as shadows as the particles scatter the light. The Abakus produces results in [counts/sec] so a flow-meter is attached to the setup so a [counts/cm] can be calculated.

In springtime dust is carried by storms from Asia. This is known from the atmosphere circulation and the composition of the dust, more about this later in the chapter. Dust and volcanic tephra in the atmosphere scatter light and reduces the solar insolation. Dust particles also provide the base for atmosphere chemistry reactions and an annual signal.

3.3.5. Sodium

Sodium, Na^+ , is a part of sea salt sodium chloride $NaCl$. As powerful storms rage around the Greenland coast during the winter, sea spray is blown on to the ice sheet. This fact makes it possible to detect an annual signal in the ice core as the sodium concentration is higher in the winter.

There are other sources of Sodium, so to calculate the non-seasalt (nss) signal the amount of Chloride is measured, this is the seasalt(ss), and subtracted from the total amount (tot). $[nss] = [tot] - [ss]$.

In the CFA it is measured by adding a reagent to the sample. The sample and reagent are mixed in a 0.5m tubing bound in a coil for maximum mixing. After this mixing it goes through an *Accurel microporous membrane*, what allows air but not water to pass through, and then into an IMER column. This is a *IMmobilised Enzyme Reactor*, that adds enzymes to the sample, this is again mixed with a buffer solution that stabilises the reaction. The sample is subjected to light at a wavelength of 410nm, and is detected with the absorption method.

3.3.6. Ammonium

Ammonia, NH_4^+ , is very important for atmosphere acid-based chemistry. It is released in biomass burning, from soil and decomposition [Anklin *et al.*, 1996]. It is mostly a summer signal as forest fires usually happen during the summer.

It is measured by adding a reagent to the sample. The sample and reagent are mixed in a 0.5m tubing bound in a coil for maximum mixing. After this mixing it is heated to $85^\circ C$ for the chemistry to work and cooled to $20^\circ C$ before going through a *Accurel microporous membrane* what allows air but not water to pass through, and then exposed to light at 365nm where it fluoresces at 420nm. This is the fluorimetric detection.

3.4. Output from CFA

Figure (3.4.1) is an example of CFA data output. The parameters used to identify the annual signals included visual stratigraphy³, conductivity, and dust concentration. Annual layers in sodium were not observed due to diffusion in the ice as well as the limited sampling resolution. Annual cycles in ammonium were identifiable only during the interstadials, when greater concentrations and thicker layers enabled their identification. Three people independently evaluated the data to produce three annual layer counting results. When an annual layer was uncertain, it was assigned a value of $1/2 \pm 1/2$ yr. The three independent counting results were then evaluated again to produce a consistent final counting result [Vallelonga *et al.*, 2012].

³See Figure (2.8.2) at page 27

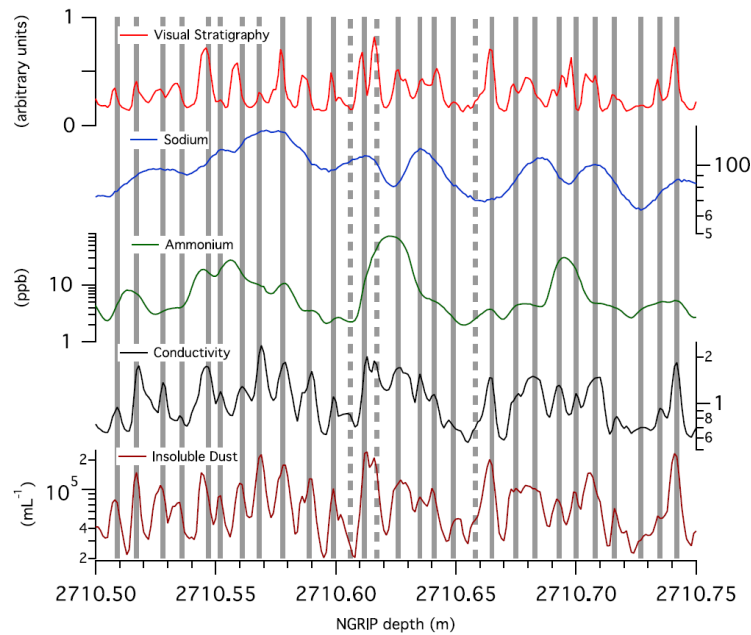


Figure 3.4.1.: Example of CFA measurements of NGRIP glacial ice and assignment of annual layers. Visual stratigraphy was measured by optical scanning at the drilling site, not by CFA. Vertical grey bars indicate "certain" (solid line) and "uncertain" (dotted line) years. Note that sodium, ammonium, conductivity and insoluble dust are plotted on logarithmic scales [Vallelonga *et al.*, 2012].

3.5. Calibration

Before and after measurements, a calibration series is run. Samples with pure Milli-Q water are fed into the system to establish the baseline, then a pulse of standards with a known concentration is injected into the system. This is seen on Figure (3.5.1 b,e). There are several reasons to do this:

Contamination If during the measurement some part of the system is contaminated, the calibration before the measurements won't fit the calibration after. Corrective measures will be done during the data processing.

Baseline shift There can be several reasons for the baseline to change, most likely some of the components, like columns, are getting worn out.

For calculations By using known concentration, one can calibrate the constants used in the algorithms calculating the concentration. Constants like ϵ in eq (3.1) on page 31.

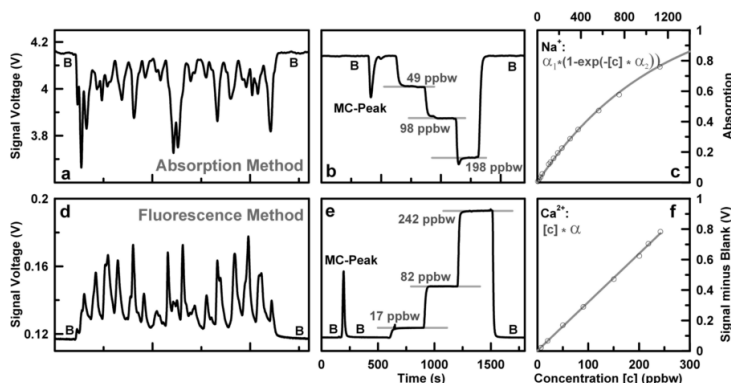


Figure 3.5.1.: Typical measurement of a 110cm ice core (a, d) and a calibration series (b, e). Na^+ is determined by an absorbance method, Ca^{2+} is measured using a fluorimetric method. The calibration series measurement (b, e) comprises also blank (B) and multicomponent standard solution (MC) signals. (c, f) show typical calibration curves and coefficients [Kaufmann *et al.*, 2008]

3.6. The impurities in the ice

There are a lot of different impurities in the ice core. Physical particles like dust and chemical traces, can each tell a story of past events. The impurity signals are proxies of climate signals. The way and methods the impurities reach the ice sheet is vital to understand what the signal tells us.

3.6.1. Transport

Before the impurities reach the ice sheet, they must be transported there from the source area. Where this area is, is limited by the atmosphere lifetime and the transport path ways. Dust aerosols particle size is primarily 0.1 to 10 μm , with a mean size of 2 μm . Such aerosols have a lifetime of hours to weeks, allowing long range transport over scales of thousands of kilometres [Jickells *et al.*, 2005]. Dust production, transport, and deposition depend on climatic factors, particularly atmospheric structure, which regulates uplift, wind speed and precipitation, which in the end influences removal. During the glacial periods, the world was much dryer, as much of the water was bound in ice, so we see dust signals in the ice two to five times greater than in the interglacial periods.

The source area from dust located in the ice cores have been identified as Asian in origin. By comparing the isotopic composition of the dust found in the Greenland ice cores, with that of deserts and dust sources in the Northern hemisphere, see Figure (3.6.1), the dust source is China or Mongolia. Due to their different geological histories, the dust source areas have different isotopic fingerprints in the elements of Strontium (Sr) and Neodymium (Nd). The presence of volcanic ash in the ice core will influence the data towards "Circum Pacific Volcanic Rocks" [Svensson *et al.*, 2000].

3.6.2. Dry and wet deposition

The rate of deposition depends on several processes, most important dry and wet deposition. Decomposition by atmospheric chemical and photochemical processes is also a possibility.

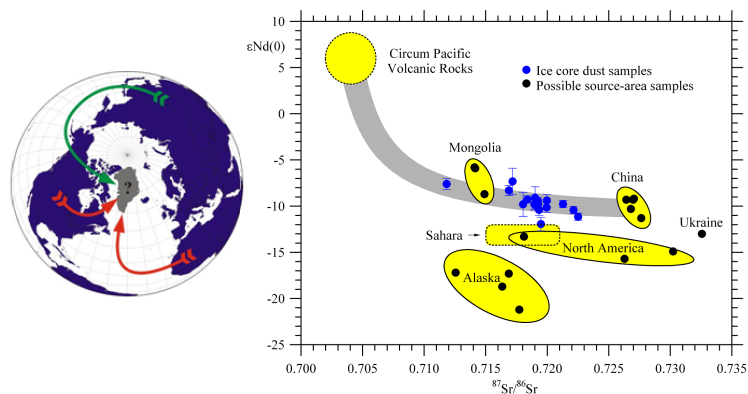


Figure 3.6.1.: To identify the origin of the dust, the isotopic composition is analysed. The blue dots represents the isotopic Strontium (Sr) and Neodymium (Nd) ratio in the ice cores measured. Of these the oldest is 45.000 years old. The isotopic composition of the dust found in the ice cores suggest that the dust is of Asian origin. Figure by [Svensson *et al.*, 2000].

Dry deposition is mostly caused by gravitational sedimentation, this fallout is mostly mineral dust and volcanic Tephra, especially particles larger than $5 \mu\text{m}$ will tend to settle fast and therefore less likely to be found on the centre of the ice sheet. This deposition is independent of the snow accumulation.

Wet deposition is caused by precipitation, condensation nucleus or scavenging traces caught by the falling snowflake.

3.6.3. Concentration Vs. Flux

When the CFA is running it measures results in concentration [ppb], [ng/g], [mg/m^3], and so on. To put it into context the precipitation has to be taken into account. This gives the fluxes [mg/m^3] \times [m/yr] = [$\text{mg/m}^2/\text{yr}$]. The amount of precipitation in general influences the amount of impurities in the atmosphere. Heavy precipitation cleans the atmosphere, and the amounts of impurities that reach the ice sheet decreases.

3.7. The Bern CFA system

The fieldwork at NEEM, was done on the Bern⁴ CFA system and the data analysis is done on their data. The main difference between the Copenhagen system and the Bern System is that the Copenhagen system measures fewer components than the Bern system, but with much greater resolution. This also means that the melt speed is almost twice as slow $\approx 8\text{mL}/\text{min}$ in Copenhagen as it is in Bern $\approx 15\text{mL}/\text{min}$. Figure (3.7.2) shows a schematic of the Bern setup.

Aside from Conductivity, Dust, Ammonium and Sodium, the Bern CFA also measures

Hydrogen peroxide (H_2O_2) a major atmospheric oxidant and contributes to the oxidizing capacity of the atmosphere along with the hydroxyl radical (OH) and ozone (O_3) [Frey *et al.*,

⁴Climate and Environmental Physics, Physics Institute, and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

2006; Lamarque *et al.*, 2011].

Sulfate (SO_4^{2-}) has a constant background signal. The interesting aspect is volcanic eruptions show up with a significant signal under normal circumstances. With these signals the age of the ice can be synchronised with other historic records. [Bigler *et al.*, 2007; Kaufmann *et al.*, 2010]

Formaldehyde ($HCHO$) is linked to the OH radical concentration, which to a large extent determines the atmospheric oxidation capacity. The oxidation capacity determines the atmospheric lifetime of many trace species that influence the radiation balance and therefore the climatic conditions [Fuhrer *et al.*, 1993].

Nitrate (NO_3^-) The preservation of nitrate in the ice is believed to be determined by; snow accumulation, local temperature, in situ physiochemical reactions, temperature dependent partitioning between the air and ice, and pH-dependent mobility of the ion in ice. [Burkhardt, 2004]

Calcium (Ca^{2+}) which is a soluble dust signal, just like the insoluble dust.

The acidity (pH) The acidity of the ice.

3.7.1. Resolution

Bern looks for a lot of components at the cost of resolution, while we in Copenhagen only look at a few but with a much higher temporal resolution. At Figure (3.7.1) there are a lot more details in the C CFA (Copenhagen CFA) than in the B CFA (Bern CFA). More detectors needs more of the sample water.

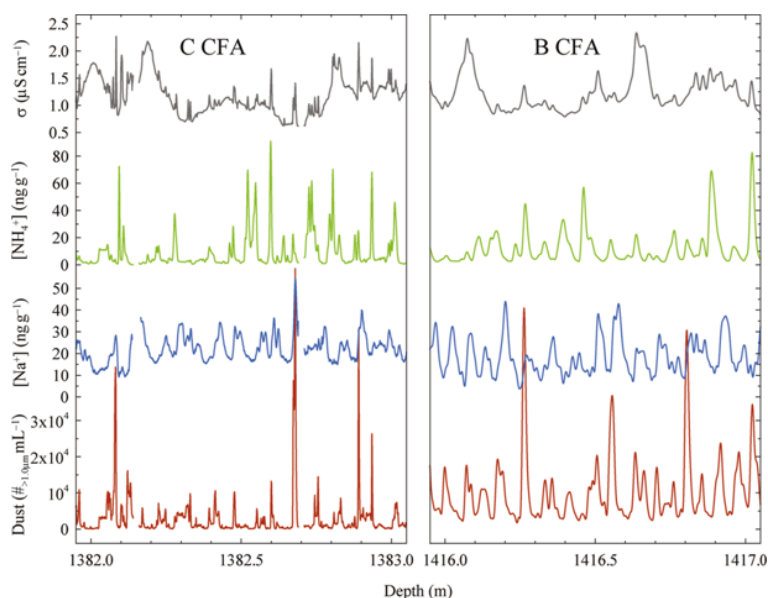


Figure 3.7.1.: C CFA is the Copenhagen CFA output, while B CFA is the Bern CFA output. While Bern CFA can measure a lot of components it does so on the cost of resolution. σ is the conductivity. Figure by [Bigler *et al.*, 2011].

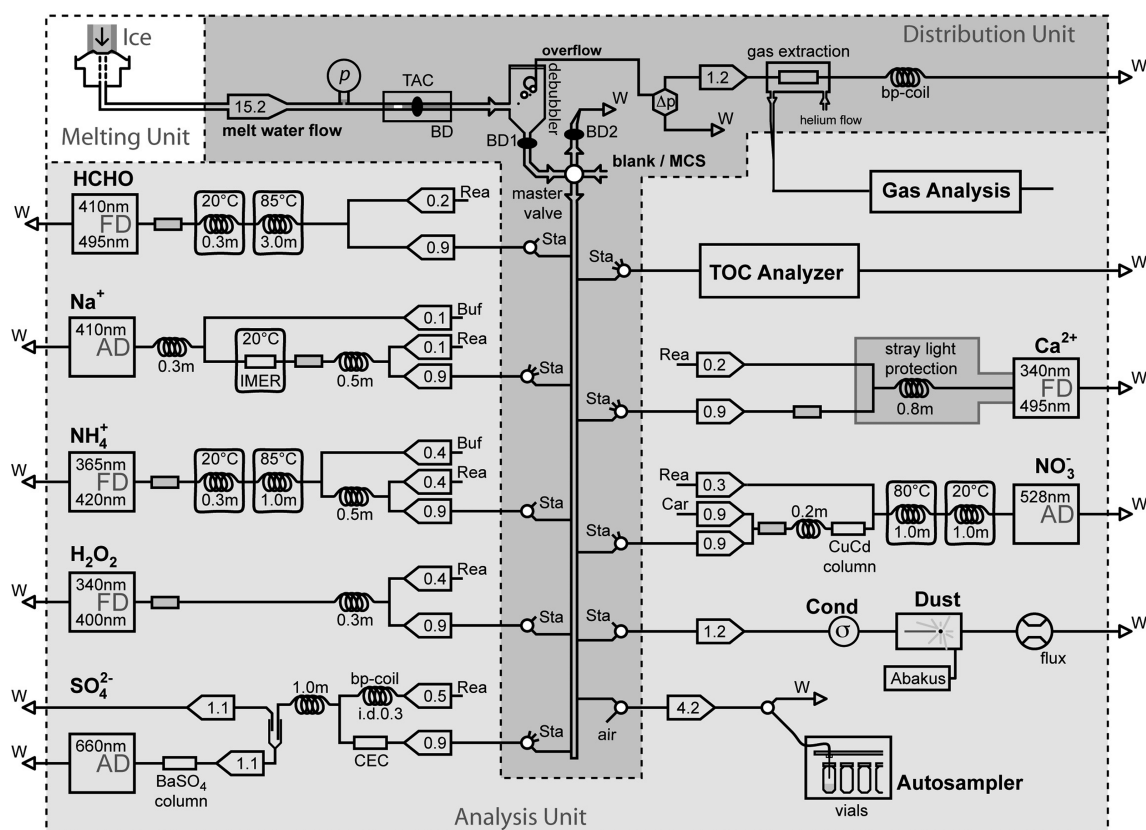


Figure 3.7.2.: The Bern setup. The ice melts at the melt unit, and enters the distribution unit, where it is divided by a debubbler into bubble free sample, and an air filled overflow that can be used for gass analysis. The sample goes through a master valve and is distributed to the different measuring systems.

Abbreviations and symbols: total air content (TAC), Solenoid valves (small white circles), bubble detectors (BD, black ellipses), pressure gauge (p), pump tubes and flow directions (arrow boxes), flow rates in mL/min (numbers in the arrow boxes), Accurel micro porous membrane debubbler (small gray boxes), fluorimetric detection (FD), absorption detection (AD), standard solution (Sta), reagent (Rea), carrier solution (Car), buffer solution (Buf), waste (W), immobilized enzyme reactor (IMER), cation exchange column (CEC), multicomponent calibration solution (MCS), buffer volume for pressure decoupling (Δp), and back pressure coil (bp-coil). Furthermore, lengths and temperatures (if heated or cooled) of mixing and reactor coils, and wavelenghts of the different detections are indicated in the figure [Kaufmann et al., 2008]

4. Drill liquid detection

To detect the drill liquid several ideas were discussed, since no one in known literature had done this before¹. The most optimal approach would be if the drill liquid was detectable by optics alone. This would make the detector non-invasive on the complex CFA system. If this was not possible, the drill liquid detector should have a separate line, where a reagent and possible buffer could be added, so the drill liquid react and becomes detectable. Fortunately the drill liquid could be detected by UV light alone.

To make this detector the following was used:

Genesys 10UV Spectrophotometer (Thermo Scientific, USA) is a easy-to-use device that can scan a liquid sample for its absorbents/transmittance. A range of up to 100nm is set, a baseline is measured and then the unknown sample(s). It is self calibrating and with glass curvettes the wavelength range is 320-1100nm, with Quartz curvettes (Hellma Analytics, Germany) the range is 190-1100nm. The CIC had some of these rather expensive Quartz curvettes in store, so these curvettes were used right from the beginning.



Drill liquid At NEEM *Estisol 240* (Coconut oil extract) and *Coasol* (ester mixture) was mixed, 2× *Estisol* to 1× *Coasol*. See section 2.7, page 25 for more details. At NGRIP a compound called *D60/HCFC 141b* was used as drill liquid. A new drill liquid that is still in testing, and was field tested at NEEM 2012 is *Estisol 140*. These drill liquid samples were acquired for this experiment.

Milli-Q water (Milli-Q, $\geq 18.2\text{M}\Omega/\text{cm}$, Millipore Advantage) In the CFA system Milli-Q water is used due to its extreme purity, as blank water for baseline calibration and cleaning by flushing the system.

Melted ice During several CFA measurements discreet samples are taken and from this ice

¹This author have later leaned that drill liquid detection is being done post-processing, through a complicated and time consuming chemical process that indicates if the discrete sample was contaminated or not.

water samples from NEEM S1 2007-93 (shallow core, firn ice, a depth of $\approx 10m$), NGRIP 4914 and NGRIP 4916 (ice from a depth of $\approx 2706m$).

The *Genesys 10UV Spectrophotometer* was setup with the quartz QS1000 cuvettes. Since the Milli-Q water is used as baseline in the CFA system, it was also chosen for the baseline in the spectrophotometer. Connected to a computer that has *VISIONlite Scan 1.0* software (Thermo Spectronic 2002) the spectrophotometer can scan a sample 100 nm of the spectrum at the time. The spectrum range is entered into the spectrophotometer, then it asks for the blank sample, the curvette with the Milli-Q sample is placed into the spectrophotometer and the lid is closed. This is for the relative absorption calibration. After the spectrophotometer has scanned the blank sample, it will ask for the measurement sample, the curvette with drill liquid is exchanged with the Milli-Q sample, the lid is closed and the scan begins. Likewise the ice core water was scanned. The result can be seen on Figure (4.0.1). After the initial results the NEEM and NGRIP drill liquid was scanned again to confirm.

Later when *Estisol 140* was scanned, a problem with the computer interface occurred, so the spectrophotometer was operated manually without computer connection. From 190 nm to 350 nm reading was done at 1 nm interval, at 350 nm to 900 nm, scans were done at 50 nm interval and at 900 nm to 1100 nm, scans were at 10 nm interval. From 195 nm to 263 nm the spectrophotometer absorption readout was >3 and therefore not an exact readout, hens the dotted line.

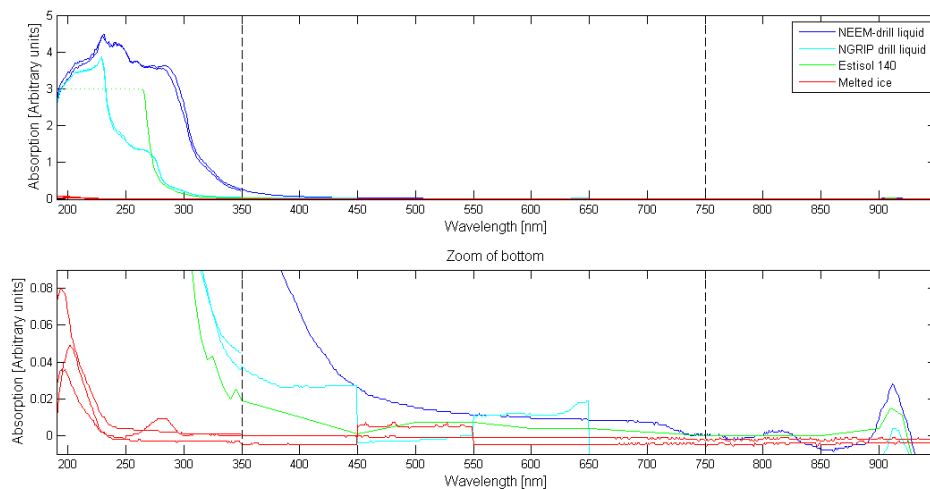


Figure 4.0.1.: A scanning with the spectrophotometer, of the ice water and drill liquid though the light spectrum. The two vertical dashed lines indicate the boundary between the UV spectrum, the visible light and the Infra Red. The *Estisol 140* readout was >3 between 195 nm and 263 nm.

As it is seen on Figure (4.0.1) the absorption from 350 nm to 750 nm is close to zero, which is as expected since the tested liquids are clear. In the UV spectrum the drill liquid absorbs more than 50 times the amount of ice core water. This means that it is possible to make an optical detector based on UV light, that will react to the drill liquid and not the melted ice.

4.1. The drill liquid detector

Since NGRIP, NEEM and *Estisol 140* drill liquid absorbs a lot of the UV light, an optical drill liquid detector was build. The flow cell, Figure (4.1.1) features a hand blown Quartz glass tube held in a plastic frame by silicone tubing. A broadband deuterium halogen light source (*DT-Mini-2-GS, Ocean Optics*) was mounted perpendicular to the Quartz tube using an optical fibre, with the other end of the optical path connected to a *USB2000 UV-VIS* spectrometer (*Ocean Optics, USA*). The program *OOIBase32, (Ocean Optics, USA)* was set to monitor at $\lambda = 290.00$ nm, that is the optimal wavelength for UV absorption delivered by the light source. The flow cell is mounted so that the water flow is vertically upwards to avoid air bubbles getting trapped in the optical path.

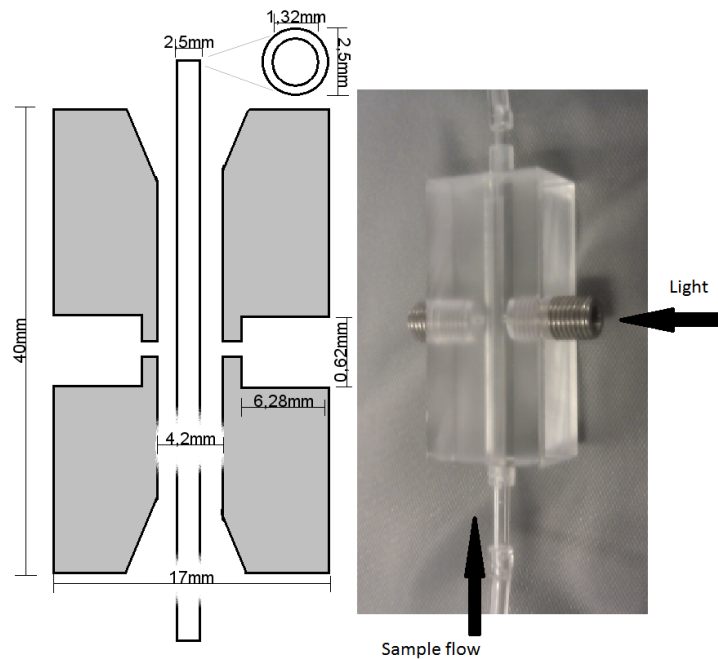


Figure 4.1.1.: The detector is made of a plastic frame (gray), where a quartz tube is held in place by some silicone tubing that fix it in place due to the cone shaped endings. The light source shines perpendicularly through the tube to the spectrometer connection. The cell is mounted vertically with the flow upwards to avoid air bubbles getting trapped in the optical path.

It was observed that if an air bubble got into the detector it would react just like drill liquid, by lowering the light intensity (counts).

To counteract this interference from air bubbles, another wavelength $\lambda = 435.83$ nm was also monitored. In this visible light, the air bubble has a recognisable feature that could be identified in the data processing, as it lowered the light intensity (counts) more than the drill liquid did.

The *Open Optic software* produce ≈ 3 measurements pr second, all which was imported into a *Matlab* script, written by this author, to analyse the data.

The script, found in the Appendix, would identify absorption as dips in the light intensity

(counts) at $\lambda = 290.00$ nm and $\lambda = 435.83$ nm.

An air bubble would lower the intensity, properly by scattering the light, to a value lower than 1500 counts at $\lambda = 435.83$ nm. The script would then identify a drill liquid detection when $\lambda = 290.00$ nm shows an absorption and $\lambda = 435.83$ shows an absorption above 1500 counts. This would be indicated with a circle mark on the graph as seen in Figure (4.1.2).

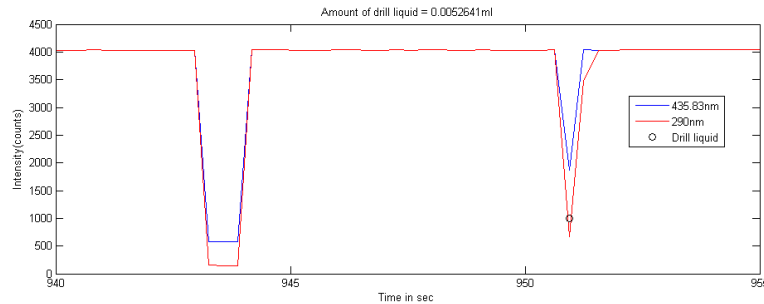


Figure 4.1.2.: The Matlab script identifies possible drill liquid and marks it with a black \circ . First an air bubble and then a droplet of drill liquid.

4.2. The experimental setup

When running lab test of the detector the setup is was as the depicted at Figure (4.2.1).

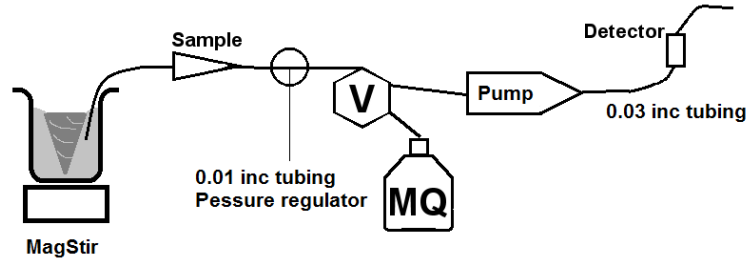


Figure 4.2.1.: From the magnetic stirrer a sample of drill liquid droplets in varying sizes and water is pumped towards the detector. Past a pressure regulator where excess water goes to waste. At the valve (V), Milli-Q water (MQ) can also be pumped into the detector if no sample is available.

MQ The ultra clean Milli-Q standard water that keeps air out and rinses the system.

Sample A magnetic stirrer mixes the water with the lighter drill liquid, in a way that lets drill liquid enter the system randomly. Depending on the speed of the stirrer, the drill liquid droplets can enter the detector at different sizes. This setup also prevents air bubbles from getting into the detector.

Tubing The Tubing was Polymer tubing (HPFA) and had an outer diameter of 1/16 inch and an inner diameter of 0.03 inches with the only exception at the pressure regulator waste line that had 0.01 inch internal diameter. Flangeless fittings were used for connection between tubes.

Pressure regulator is a small device that prevents a pressure build up in the system. If the line-in carries a bigger flow than the line-out can carry, then the excess water flows out to waste and keeps the pressure in the system constant. The pressure regulator was a mandatory add-on to the detector when it was connected to the BERN CFA. Pressure build up have previous resulted in lines disconnecting during melt and measurements.

Peristaltic Pump 0.5 ml/min flow in lab test. At NEEM the flow was 1.2 ml/min. The yellow-orange pump tubing has a inner diameter 0.48mm.

Light source is a Deuterium lamp that gives a light from $\lambda \approx 177nm$ to $\lambda \approx 880nm$.

The flow cell See Figure (4.1.1) at page 41.

Spectrometer monitors two wavelengths $\lambda = 290.00$ nm and $\lambda = 435.83$ nm.

Figure (4.2.2) shows part a test measurement where a magnetic stirrer mixed Milli-Q water and drill liquid, in a way so drill liquid droplets would enter the system randomly with a minimum of air bubbles.

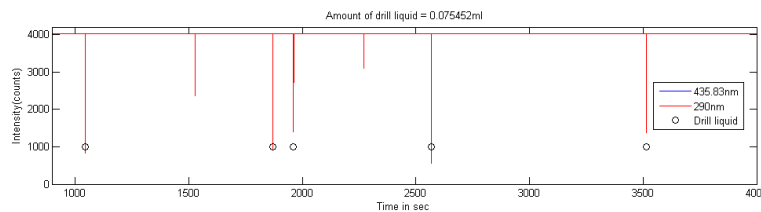


Figure 4.2.2.: The Matlab script identifies possible drill liquid and marks it with a black \circ . Those dips not marked are air bubbles.

4.3. Drill liquids effect on the tubing

During the development of the detector an important observation was made. The drill liquid sticks to the inside of the tubing. A drill liquid droplet was spotted in the tubing and it was observed to shrink as it made its way towards the detector, see Figure (4.3.1).

This coating of the tubes insides can change the flow rate, can introduce turbulence, and possible interferes with the mixing of sample and reagents. Drill liquid can also stick in the fittings, filters and columns thus resulting in measurement artefacts. Stuck drill liquid can also sit for some time before dislodging, introducing a randomness to the contamination.

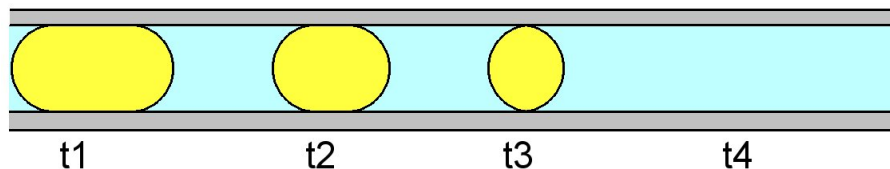


Figure 4.3.1.: A visual observation of the drill liquid, showed how a droplet of drill liquid got smaller and smaller while travelling in the tubes (t1 to t3) until it finally disappeared (t4). The drill liquid sticks to the inside of the tubing, and during it's travel, it deposits more and more drill liquid until there is no more, or it reaches the instruments.

5. Measurements in the field

The drill liquid detector was brought into the field at NEEM 2011 (77°45'N 051°09'E, 2480m asl, www.neem.dk) to be tested during the measurement of the brittle ice. The detector was setup in parallel with the other detectors in the BERN CFA system, see section 3.7 on page 36.

5.1. Loading and preparing the ice

While at NEEM, it was this authors job to prepare the ice for the CFA. The ice from the brittle zone had been relaxing since 2009 and had at that time been cut into 3.5 cm × 3.5 cm × 110 cm and stored in aluminium trays for support of the more fragile ice cores.

The ice core was unpacked from its bag and if there were breaks, the pieces were put back together so the ice core could be measured with a ruler. As this ice was brittle ice there were a lot of breaks and some of the breaks were refrozen. If there were cracks or breaks in the ice, the ice was marked for a perpendicular cut as close to the crack as possible. The distance from the bottom of the core to the cuts was measured as B1-B2, B1-B3, B1-B4 as seen in the Figure (5.1.2) example. This information was noted on the cutting sheets, including the length of the Milli-Q ice cube at the very bottom of the sample. Only intact pieces of ice longer then 10 cm would be used in the CFA. Even ice with refrozen cracks was discarded as sample ice as the risk of drill liquid contamination was to high.

The useable pieces were cleaned and fit inside the ice core tray. The ends were cut perpendicular to the core and levelled with a plane. From this point on the levelled end was treated as sterile. The melt head was cleaned with *Isopropanol* ($((CH_3)_2CHOH)$ mixed 1:1 with Milli-Q water) and the ice core tray was loaded onto the melt head. The CFA operator would enter the cutting information into the computer and then the melting began.

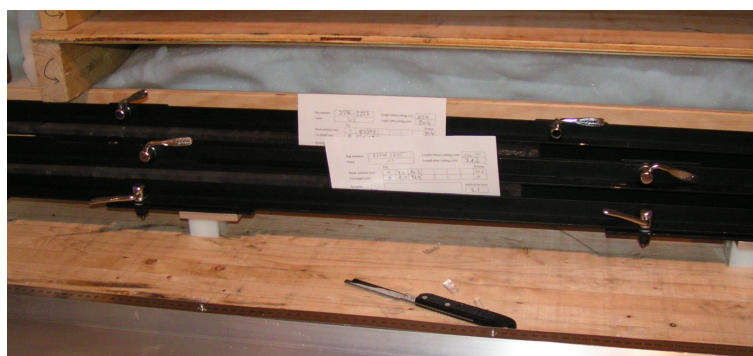
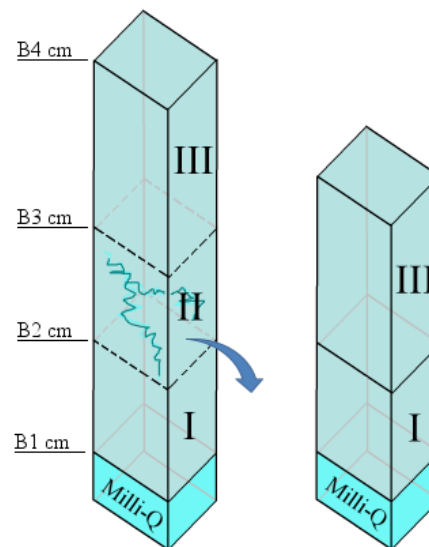


Figure 5.1.1.: Two trays of ice, prepared for melting, with detailed cutting sheets attached.

Figure 5.1.2: An example of how a ice core is readied for CFA measurement. The crack is identified and marked out for cutting. The length from the bottom to the cuts B1, B2, B3 and B4 are noted. The length of the cutaway piece (II) can then be calculated and this is used in later data processing.



5.2. What to expect from drill liquid contamination

Discussing the drill liquid's effect on the CFA with Gideon Gfeller, the night shift CFA operator from Bern, led to the following exceptions of drill liquid contamination. When drill liquid hits the BERN CFA system the expected reaction is listed in Table (5.1).

Table 5.1.: The expected effect of drill liquid on the BERN CFA, [Gfeller, 2011]

Chemical component	Expected reaction
<i>Conductivity</i>	Counts drop as this measures all ions
<i>Dust</i>	Counts rise
NH_4 - Ammonium	Unknown
H_2O_2 - Hydrogen peroxide	Unknown
SO_4^{2-} - Sulfate	damaged column, drill liquid gets stuck
Na^+ - Sodium	damaged column, drill liquid gets stuck
$HCHO$ - Formaldehyde	Unknown
NO_3^- - Nitrate	Damaged column, counts go up with a tail due to lingering effects
Ca^{2+} - Calcium	Unknown
<i>pH</i>	Counts go up, disturbs it somehow

5.3. Online measurements

The detector was connected to the Bern CFA system in an 8-way split mounted vertically. The drill liquid detector line was connected to the top of the split at the blue fitting in Figure (5.3.1). Since drill liquid has the density of ice, 10% lower than water, it should rise upwards, increasing the chance that drill liquid in the system would go to the drill liquid detector. In the later data processing there were a few drill liquid events that could not be aligned with contamination spikes, indicating that the drill liquid only made it to the detector.

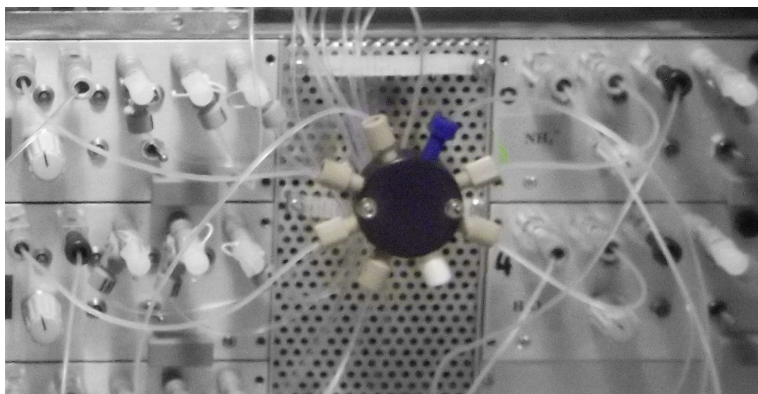


Figure 5.3.1: The drill liquid detector is connected in parallel to the other Bern CFA detectors in the 8-way split. The blue plug is the line connected to the drill liquid detector.

During the measurement period of the brittle ice, several attempts were made to add a conductivity meter, just before the drill liquid detector to ease the later data alignment, but without any luck. In the end, when the Bern CFA system was started automatically, the drill liquid detector was started manually. This would pose a challenge later during the data analysis, but since the effects of drill liquid contamination, presented in Table (5.1), it should be possible to identify drill liquid contamination.

In the total of 158 CFA measurements with the drill liquid detector running in parallel, 27 were found with at least one count of drill liquid present. Typically one or two counts of drill liquid was detected in these drill liquid events.

The amount of drill liquid in the system is approximated by taking numbers of seconds counted with drill liquid multiplied by the flow rate [ml/min]. From the melthead the lines were divided into seven individual lines for the different measurements. Assuming that the drill liquid spread evenly in these lines the total drill liquid amount in the system:

$t_{drillliquid} \times \frac{flow_{ml}}{60sec} \times 7 = ml$. With this information, ways of removing the drill liquid will be explored in Chapter 8.

5.4. Offline measurements

The drill liquid detector was removed from the Bern CFA to conduct some offline measurements to test if the detector system worked. The ice cores used for CFA measurement were cut perpendicularly, the small pieces of cut-away-ice that came from near perpendicular cracks and other pieces of the ice that could not be used for CFA measurements were used for this offline experiment, as these probably were contaminated by drill liquid.

These "chips" were melted and the water was put through the detector using a magnetic stirrer, marked **A** in Figure (5.4.1), to prevent the lighter drill liquid from floating to the top of the water. A line from the stirrer was connected to a valve, marked **B**, where Milli-Q water could be pumped into the system instead, when the system was running idle. The line continued to the peristaltic pump, **C**, and then to the detector, **D**. After the detector the line ended in a waste bucket, **E**. At the detector the light source **F**, and spectrometer **G**, were connected to the computer, marked **H** in Figure (5.4.1).

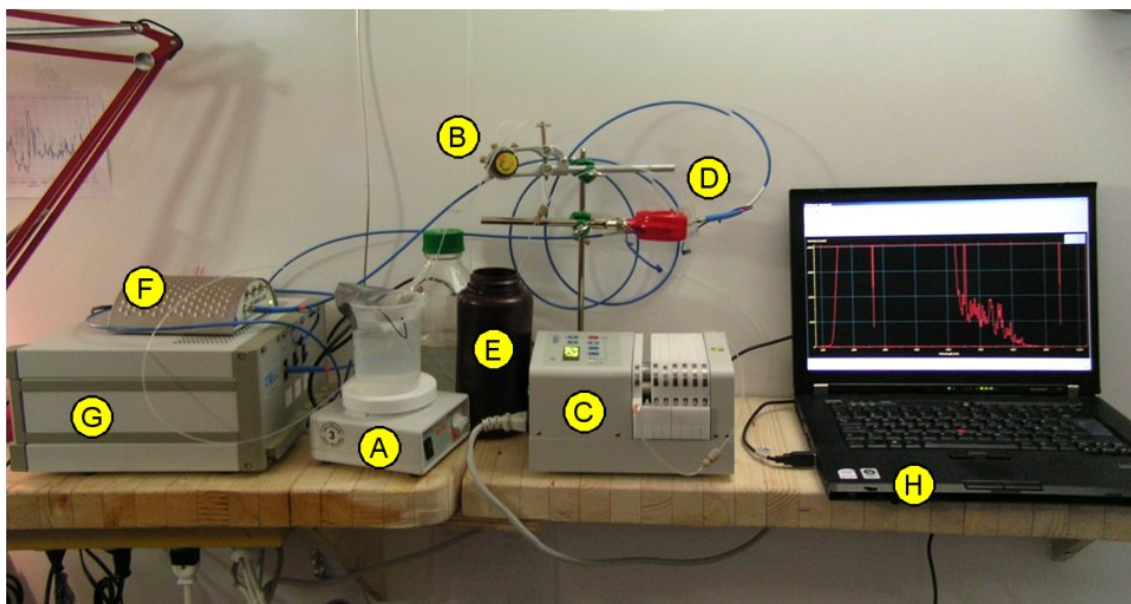


Figure 5.4.1.: The offline setup of the drill liquid detector. **A** The magnetic stirrer, that prevents drill liquid from rising to the surface. **B** the valve, **C** the peristaltic pump, **D** the detector, **E** the waste bucket, **F** the light source, **G** the spectrometer, and **H** the computer with the readout.

In figure (5.4.2) the result of the off-line measurement is presented. Drill liquid was detected along with something "Else", that did not behave as drill liquid did in the lab test. A reaction on $\lambda=290.00$ nm but with out any reaction on $\lambda=435.83$ nm.

This *unknown compound* that did not react as pure lab grade drill liquid, could be a part of the "Real recycled drill liquid". The lab drill liquid is composed by Coasol and Estisol, but does not include metal fragments or other debris from the drill and drilling process. This could account for this unknown compound that reacted to the UV light ($\lambda= 290.00$ nm) and not to the visible ($\lambda= 435.83$ nm).

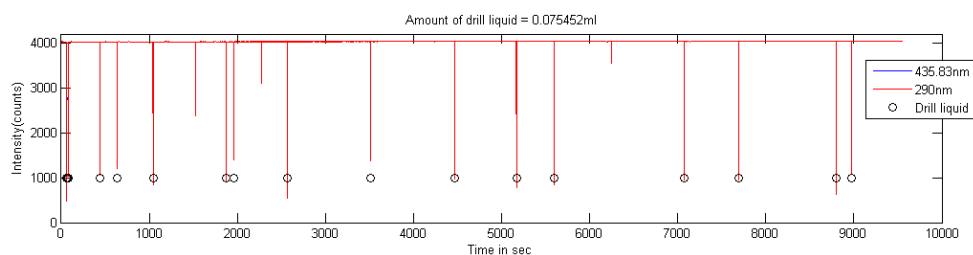


Figure 5.4.2.: Cut-away chips from the brittle ice, were gathered, melted and tested to the conclusion that "Real drill liquid" could be detected. An unknown compound was also found, which did not react as an air bubble, or as drill liquid did in the lab.

5.5. The unknown compound

In the measurements drill liquid and bubbles were detected. Lab tests, in chapter 4, had determined how these events would show up in the detector and they could be recognised. In the field a third event was detected, not behaving as an air bubble or drill liquid, as shown in Figure (5.5.1). What actually was observed by the detector was something absorbing the UV light, but not absorbing/bending the visible light as a bubble or the water/drill liquid interface does.

At first glance the cleaning fluid used to clean the melthead between measurements was a suspected candidate to the unknown detections, but other UV absorbent material, instrument error, or the recycled drill liquid it self could be the reason for these reactions.

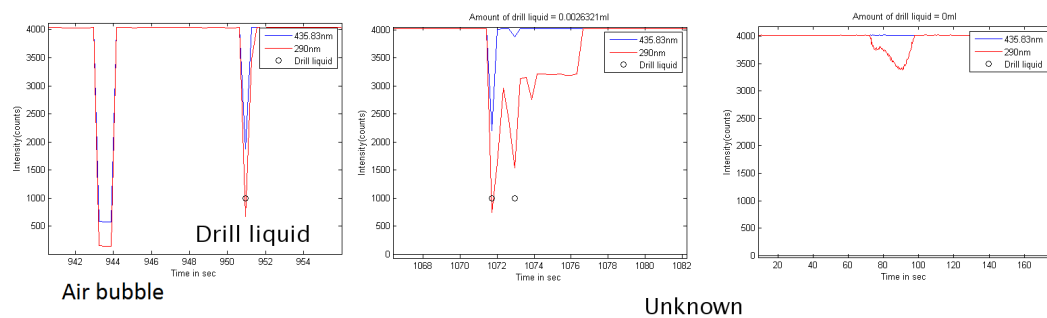


Figure 5.5.1.: The detector monitors light absorptions at two wavelengths, UV ($\lambda=290.00$ nm, red) and visible light ($\lambda=435.83$ nm, blue). An air bubble scatters more light than drill liquid absorbs at $\lambda=435.83$ nm. But there are some events that do not act as air bubbles or drill liquid as seen in the second and third graph.

5.5.1. Cleaning fluid

The Bern CFA uses *Isopropanol* ($(CH_3)_2CHOH$) mixed 1:1 with Milli-Q water, for cleaning the melt head. To test whether or not the cleaning agent was the cause of the unknown signal, a test with isopropanol was done. This test was done after the measurement of the ice chips (see section 5.4). The detector and the tubings was expected to be contaminated with drill liquid. The magnetic stirrer was replaced with a small bottle containing isopropanol.

The result of this test is seen on the Figure (5.5.2). The isopropanol cleans the system, but most importantly between second 200-300 and 400-500 there are no signals while isopropanol is running through the detector. This means that isopropanol will not show up on the detector, only all the drill liquid residue that it releases.

5.5.2. Detection error

A reason why there was no reaction on the $\lambda=435.83$ nm wavelength, could be an offset on the detector. If the monitored 435.83 nm spike could shift a few nanometers either way this could result in the observed reaction. The solution to this would be to integrate over a larger span of ± 3 nm. This is something that can be corrected in the *Open Optic software OOIBase32* settings. But if this was the reason for the unknowns alone, they would have been expected to appear more often.

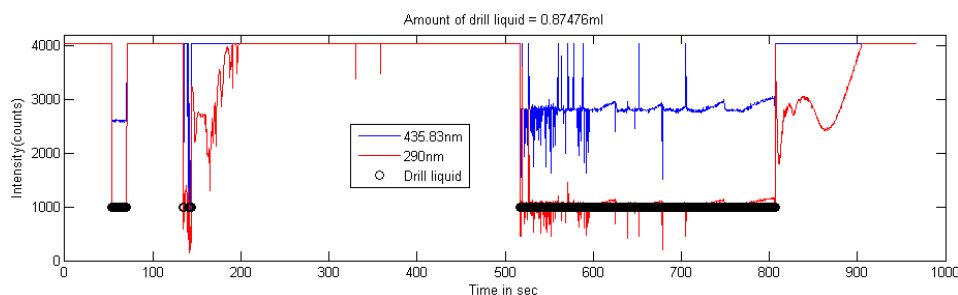


Figure 5.5.2.: After running the offline test of the detector, the setup was most likely contaminated with drill liquid. To test if the cleaning agent, isopropanol was the unknown compound, a sample of isopropanol was measured. As it does not react at time 200-300 and 400-500, it can be deduced that isopropanol is not the unknown compound. But it do clean out the drill liquid in the setup.

5.5.3. Some organic material

Organic material reacts to the UV light, but this is the middle of the ice sheet and the ice has been down there for 4000-10000 years. It is highly unlikely that there would be this much detectable organic material. Nose dripping during the preparation of the ice, would be on the outside of the ice that all ready goes to waste at the melt head.

5.5.4. Recycled drill liquid

When the ice core drill cuts down deep into the ice, the drill liquid acts like a lubricant, transporting the ice chips into the chip chompers (see more detail at chapter 2). When the ice core is retrieved, the chip and drill liquid pulp is put into a centrifuge where the liquid is removed and the wet ice chips are discarded. The drill liquid is then reused. This process could alter the drill liquid properties.

- Metal shavings from the drill head or other part of the drill.
- Other kinds of residue from the drilling or drillers.
- The centrifuge process can alter the molecules in the drill liquid

A sample of the recycled drill liquid was brought back from the field, so comparative test between *Lab drill liquid* and *Recycled drill liquid* could be done. This test was however postponed as a more likely source for the unknown signal was found.

5.5.5. Drill liquid not in bubble form

The simplest and most plausible explanation for the unknown signal is that it is drill liquid, but in small droplets, so small that they do not fill the quarts tube. The reaction seen on the $\lambda = 435.83$ nm wavelength was probably due to the curvature of the drill liquid/water interface, that distorts the light resulting in a drop in light intensity (counts).

Figure (5.5.3) displays a group of signals seen during the data processing and the most likely counterpart inside the detector. Signal **A**, the air bubble that scatters the most of the light.

Signal **B** the normal drill liquid signal. The the signals previously suspected to be from an unknown compound is more likely to be a very small droplet of drill liquid **C** that is too small to scatter the visible light at $\lambda= 435.83$ nm. Or a sticking droplet that drags a tail of drill liquid behind itself **D**.

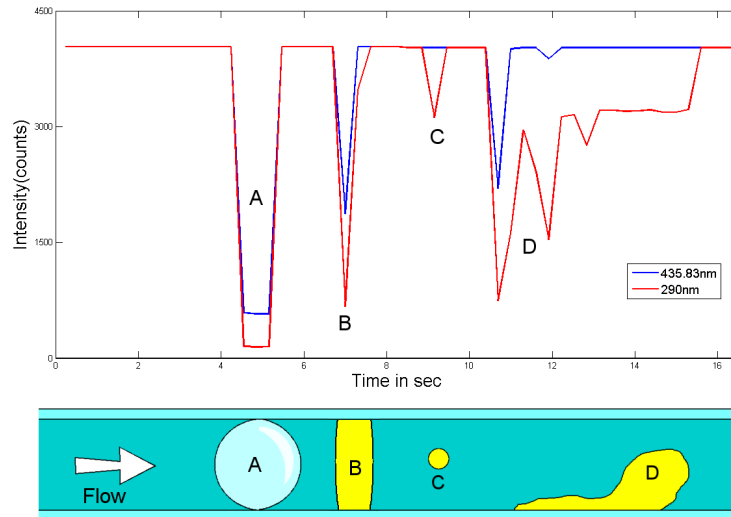


Figure 5.5.3.: By monitoring two wavelengths, drill liquid ($\lambda=290.00$ nm) and air bubbles ($\lambda=435.83$ nm) can be distinguished. Signal A with a $\lambda=435.83$ nm intensity lower than 1500, is an air bubble. Signal B is a typical example of drill liquid detection. Signal C is drill liquid in the form of droplets and signal D is a drop of drill liquid that sticks to the side of the tube, partially absorbing the UV light as it leaves a tail along the side of the Quartz tube.

6. Data Analysis

Of all the 158 measurements done with the drill liquid detector at NEEM, 27 were positive for drill liquid. In Figure (6.0.1) the distribution of the 158 measurements is shown in green along the side of the 27 positive detections showed in red. The gray span is of the brittle zone on the preliminary $\delta^{18}\text{O}$ plot from NEEM. The gaps in the measurements, green bar, is due to ice quality too poor to measure, offline measurements (see section 5.4), and a few cases of the CFA operators forgetting to start the drill liquid measurements.

The Bern CFA group was kind enough to provide raw unprocessed data for these 27 series of measurements from NEEM. A *Matlab* script was written for each of the 27 data sets, an example is found in the Appendix. First the CFA data was aligned, as there were different time delays according to the different lengths of tubing from the melt head to the respective detector. Some of the chemical components have been multiplied by an arbitrary visibility factor to make the signal identifiable. When all the chemical components have the same starting point, they are interpolated to the drill liquid detector's timescale. The CFA system measures once a second, where the detector measures 3-4 times a second. With all on the same timescale, the data is overlaid on top of each other with the drill liquid detector script's output. As an example see Figure (6.0.2). With the information from the cutting logs, the beginning and end of the ice core are marked with a black vertical dotted line, as are breaks in the ice core. The first vertical dotted line indicates the break between the ≈ 3 cm long Milli-Q ice cube and the ice core. With reference to the way the different chemical signals should react to drill liquid, Table (5.1), the drill liquid events were aligned with the CFA data.

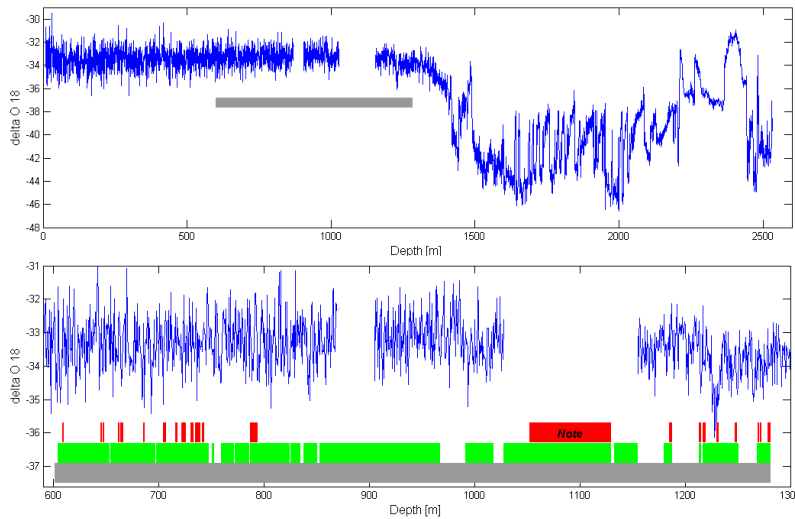


Figure 6.0.1.: The two blue graphs are the preliminary $\delta^{18}\text{O}$ plot from NEEM, with the brittle zone indicated by the grey bar. The bottom graph is the same brittle zone, but showing at which depth drill liquid measurements (green) were taken and at which depth drill liquid was detected (red).
 Note: due to low ice quality this measurement covered ≈ 78.1 m of ice, compared to the normal ≈ 1.1 m.

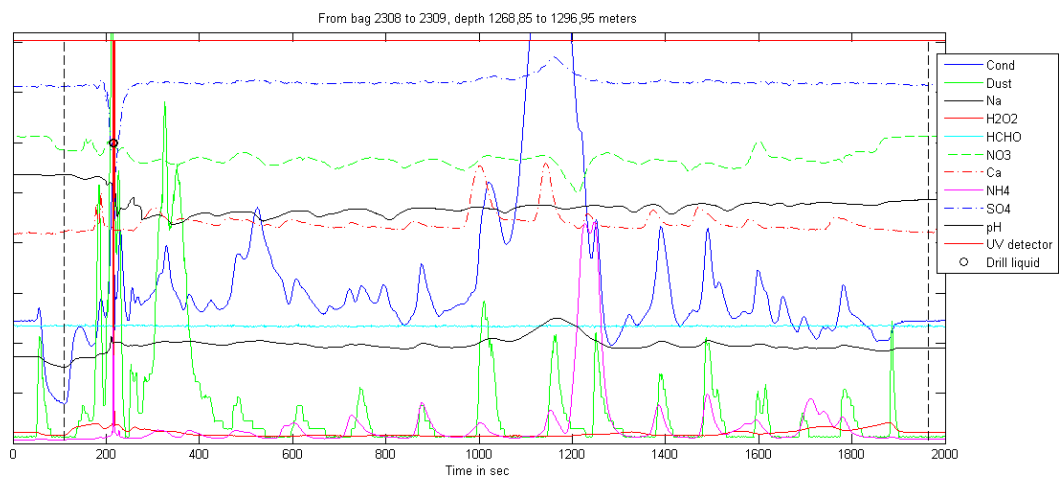


Figure 6.0.2.: The raw CFA data from NEEM, bag 2308 and 2309, depth of 1268.85 to 1296.95 m, multiplied by some arbitrary visibility factors so all the signals are visible. The drill liquid is detected and marked with a black "o". The vertical dotted black lines indicate breaks in the ice.

7. Results

All the 27 positive drill liquid detections were processed as described in Chapter 6. To see the final results the different chemical signals were plotted by it self with the drill liquid events marked as a vertical bar, and the break as a dotted vertical line. The following figure is one of these. This example is cherry piked as only 2 out of the 27 had reaction in the sulfate.

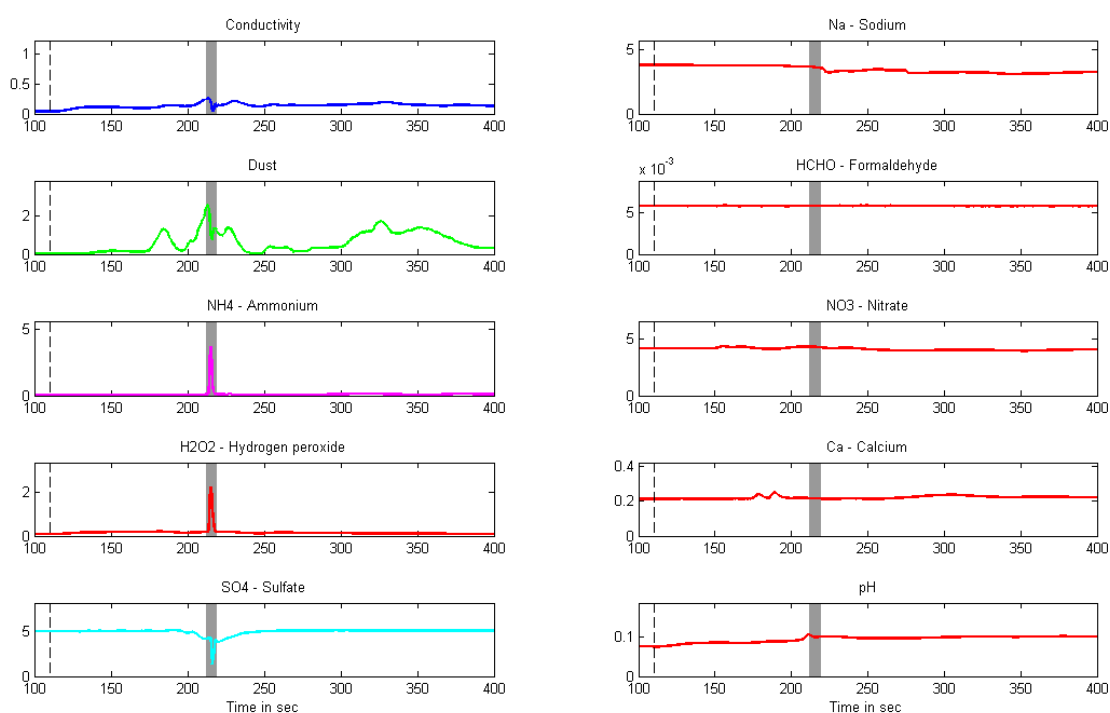


Figure 7.0.1.: The components that react to the drill liquid. The grey vertical bar indicates drill liquid contamination, and the break as a dotted vertical line. This sample is from bag 2308-2309, a depth of 1268.85 to 1296.95 m. The left column shows the different CFA components that react to the drill liquid. The CFA components in the right column never showed any reaction to the drill liquid. The y-axis of the different components are the arbitrary units from their respective detectors.

Conductivity The electric conductivity cell measures the free ions, through a flow cell with two electrodes [Bigler *et al.*, 2011]. When the low conductive drill liquid passes the detection cell, the counts drop.

Dust The dust detector measures the signal attenuation of laser light through an aperture caused by shadowing of the particles in the liquid stream. The drill liquid droplets absorb/scatter much of the light and the dust counts become artificially high as observed for the deepest NGRIP ice [Svensson *et al.*, 2011].

Ammonium NH_4 is detected by fluorescence, where the sample is excited by light at a wavelength 365 nm, and fluoresces at 420 nm [Kaufmann *et al.*, 2008]. The presence of drill liquid, results in an erroneously high concentration.

Hydrogen peroxide H_2O_2 is detected by fluorescence, where the sample is exposed to light a wavelength 340 nm and fluoresce at 400 nm [Kaufmann *et al.*, 2008]. The presence of drill liquid interferes with the voltage signal from the photomultipliers and results in an erroneously high concentration.

Sulfate SO_4 Only two of the 27 detections of drill liquid contamination caused sulfate to show a signal drop, which indicated an increase in concentration. The sulfate detector works on absorption at 660nm [Kaufmann *et al.*, 2008], which is beyond the absorption range of the drill liquid. The sample goes through a cation exchange column [Röthlisberger *et al.*, 2000], where drill liquid might accumulate and cause interference in some way.

Formaldehyde $HCHO$ is also detected by fluorescence but a 410-495 nm and is therefore out of the range where drill liquid react [Röthlisberger *et al.*, 2000].

Sodium For Na^+ detection an immobilised enzyme reactor (IMER) is needed. The IMER is a column of enzymes coated on glass beads [Bigler *et al.*, 2007]. Such columns may become clogged by drill liquid thus resulting in measurement artefacts. This was observed at a single occasion.

Nitrate NO_3^- is measured by absorption at 528nm [Röthlisberger *et al.*, 2000], outside the drill liquid reaction range as seen in Figure (4.0.1) in chapter 4.

Calcium Ca^{2+} is measured by fluorescence within wavelengths of 326 and 495nm [Röthlisberger *et al.*, 2000]. There has been no visible reactions to the drill liquid contaminations.

pH According to Gideon Gfeller, the CFA operator at NEEM, who did his master thesis on *pH* measurements in the CFA, the counts should go up, as the drill liquid disturbs the detector that measures H^+ [Gfeller, 2011], but this was never observed.

Table 7.1.: A summarise of the CFA data's reaction to drill liquid.

Chemical component	Expected Reaction	Observed Reaction
<i>Conductivity</i>	Counts drop as this measures all ions	Counts drop
<i>Dust</i>	Counts rise	Counts rise
NH_4 - Ammonium	Unknown	Counts rise
H_2O_2 - Hydrogen peroxide	Unknown	Counts rise
SO_4^{2-} - Sulfate	damaged column, drill liquid gets stuck	Counts drop
Na^+ - Sodium	damaged column, drill liquid gets stuck	No reaction is observed
$HCHO$ - Formaldehyde	Unknown	No reaction is observed
NO_3^- - Nitrate	Damaged column, counts go up with a tail due to lingering effect	No reaction is observed
Ca^{2+} - Calcium	Unknown	No reaction is observed
<i>pH</i>	counts go up, disturbs it some how	No reaction is observed

7.1. Drill liquids effect on the chemistry itself

The drill liquid clearly has an effect on the instruments, but preliminary results from the brittle ice data analysis, indicates that the drill liquid could interact with the chemistry itself. In Bern they see a significant reduction in the Calcium signal, and they speculate that it was the drill liquid coating the inside of the tubing, see section 4.3, that absorbs some of the Calcium signal. **Daiana Leuenberger** from Bern is investigating this.

7.2. Result overview

At NEEM 27 events of drill liquid contamination were detected out of 158 measurements. These events were sorted according to where in the measurement they occurred, as showed in Table (7.2). All these results have been shared with the Bern CFA group.

Table 7.2.: The results from the drill liquid detector. The numbers of times drill liquid was detected in a particular part of the ice core measurement. Between 793.1 m and 1052.7 m, the ice was of a so low quality that it was discarded.

Bag #	Depth top (m)	bottom (m)	Length (m)	At the start	At the Milli-Q ice	In the core	At the end	After measure	In a break	Could not align	Small drill liquid	# of breaks
1107-1108	608.3	609.4	1.1	1	1							0
1173-1174	644.6	645.7	1.1			1						N/A
1177-1178	646.8	647.9	1.1			1			1			1
1203-1204	661.1	662.2	1.1		1					1	1	1
1207-1208	663.3	664.4	1.1	1	1							0
1209-1210	664.4	665.5	1.1	1	1							2
1247-1248	685.3	686.4	1.1				1	2			1	N/A
1281-1284	704.0	706.2	2.2	1	1							2
1303-1304	716.1	717.2	1.1				1	1	1		1	3
1313-1316	721.6	723.8	2.2							1	1	5
1317-1318	723.8	724.9	1.1	1	1							2
1329-1332	730.4	732.6	2.2	1	1							6
1337-1340	734.8	737.0	2.2					1				3
1341-1344	737.0	739.2	2.2	1	1							4
1349-1350	741.4	742.5	1.1		1			1			1	1
1431-1442	785.4	793.1	7.7							1	1	5
1915-1998	1052.7	1098.9	46.2			1						7
1999-2053	1098.9	1130.8	31.9	1					1		1	6
2156-2159	1185.3	1187.5	2.2	1	1							5
2206-2209	1212.8	1215.0	2.2	1					1			2
2214-2215	1217.2	1219.4	2.2	1	1							3
2238-2239	1230.4	1231.5	1.1	1					1			2
2270-2271	1248.0	1249.1	1.1			2						0
2308-2309	1268.9	1270.0	1.1			1						0
2312-2313	1271.1	1272.2	1.1			1						3
2326-2327	1278.8	1279.9	1.1	1	1							1
2328-2329	1279.9	1281.0	1.1			1			1			0

Note: Two cutting sheets were not available, therefore N/A

7.3. Bags, depths, lengths and breaks

One "bag" is 0.55 m of ice, spanning a depth section of the ice sheet. During the CFA measurements at NEEM approximately 1.1 m of usable ice was measured at the time. The number of breaks in Table (7.2) refers to the number of clean perpendicular cuts there are, when two or more pieces of ice are measured at the same time. See Figure (5.1.2) on page 46 for more information. When the ice was of the poorest measurable quality, depth 1052.7 to 1098.9 m, 8 pieces of a minimum length of 10 cm, were put side by side to be measured.

In Table (A.1) in the Appendix, the break position from the start of the ice core is noted in cm. Although the 27 detections of drill liquid are not spread evenly over the brittle zone, a Gaussian bell shape is still visible.

7.4. Detection in the beginning of the ice core

Half of the detections, 13 in total, were in the beginning of the measurement. And of these 12 were during the Milly-Q ice cube. When preparing for melting, the melt head is cleaned with *Isopropanol*, as showed in section 5.5.1, this cleans any drill liquid residue and the melting of the Milli-Q ice cube pushes water and cleaning agent through the system. At NEEM 2011, the Milly-Q ice cube were $\approx 3\text{cm}$ high. See section 5.1. Most of the contaminations (48, 15%) occurred at the start of the measurement, indicating a remnant of this cleaning. The primary conclusion is that the Milly-Q cube must not be any smaller, as any remnant drill liquid should be flushed out before the melting of the "real" ice begins.

7.5. Detection in the core

There were some detections of drill liquid during the measurement, indicating contamination in the ice core. As seen on Table (7.2) bag 1177-1178 was the only one that had a contamination in a break, between to pieces of ice. The rest of the in-core detection did not show any obvious correlation. Empirical evidence shows that some refrozen cracks, possibly harbouring drill liquid, were very hard to see when preparing the ice. That and the drill liquid sticking inside the tubing offers the only plausible explanation to drill liquid contamination within ice.

7.6. Detection in end of the core or after measurement

There were several events at the end and after a core was finished as the system was back on Milly-Q. That drill liquid lingers in the system is not surprising since it has already been observed that the drill liquid sticks to the inside of the tubes. See Figure (4.3.1), page 43. In the junctions and valves where the internal diameter is small, the flow speed is lager, and it is fair to assume that the drill liquid does not accumulate there. That drill liquid suddenly appears after the measurement is done must be the drill liquid coating in the tubes that slowly reforms as droplets and finally is released into the water flow.

7.7. Detection with out reaction

Drill liquid shows effect in conductivity, dust, ammonium, hydrogen peroxide and in a few cases sulfate. But there were some detections of drill liquid that did not show in the signals as it would be expected. The detector was connected to the BERN system at a seven split junction. Figure (5.3.1), page 47. One must assume that the sample water, with drill liquid, is divided equally at the point. But since the junction was placed vertically and the line to the detector was the top one of the seven, and given that the drill liquid has a lower density than water, it could be argued that the drill liquid would rise upwards when it had the opportunity.

It is also possible, that those drill liquid events that could not be aligned, were from the drill liquid that had coated the tubes, and then was reformed at droplets.

8. Drill liquid removal

In previous chapters drill liquid has shown to produce measurement artifacts and cause problems with the vulnerable instruments. It would be ideal to remove the drill liquid before it has a chance to cause problems as presented in the project description on page 14, different removal methods have been explored.

8.1. Passive filtering

Since the density of the drill liquid is the same as ice, around $900\text{kg}/\text{m}^3$ and water $1000\text{kg}/\text{m}^3$, drill liquid will due to buoyancy find its way to the surface in steady state condition. A method like a debubbler could work, but only with very slow flow rates. But since the drill liquid already have passed two debubblers before reaching the detector at the NEEM/Bern CFA setup, this passive filtering is given little credibility.

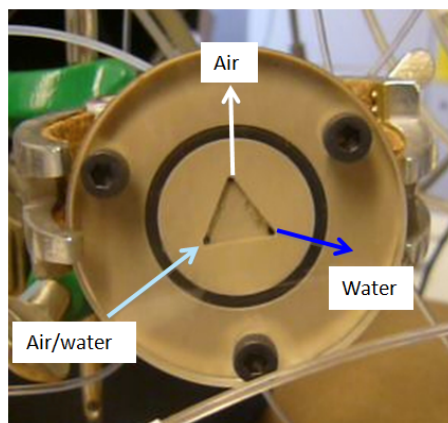


Figure 8.1.1.: A water-air mixture enters in the lower left corner, the air rises to the upper corner and pure water exits in the lower right corner. The narrow space reduces the mixing.

8.2. Active filtering

There are commercial filters that can be conditioned to pick up specific oils, but whether or not this will interfere with the other measurements is unknown. It will however certainly interfere with the flow rate, pressure, and mixing.

8.3. Mechanically filtering

A steady flow is important for the CFA system, and during a night shift in the NEEM CFA lab an idea took form. Drill liquid is so damaging to the system that to remove it was deemed

worth losing a few seconds of data. The data is lost anyway to contamination. If an automated detector was placed between the melt head and the CFA system, and this detector controlled an automatic valve the drill liquid could be derailed when it was detected. While the sample line with drill liquid is derailed Milly-Q is pumped in so the flow rate remains constant. See Figure (8.3.1).

This mechanical filtering system could help the CFA system, but it could cause problems in some of the other systems connected to the melt head, like the gas-lab. A pulse of Milly-Q water would throw the methane and isotope measurement completely off.

An active system as in Figure (8.3.1) could be placed in front of the vulnerable systems like conductivity, dust, ammonium, hydrogen peroxide and sulfate. In this way no interference would reach the other parts of the CFA.

A more passive system could be used to identify and quantify the amount of drill liquid present in the samples. Such a system could be used in cases where drill fluid coats the inside of the tubing without directly influencing detectors, and it would provide the CFA operator with an additional indication of when a full-system maintenance and cleaning is needed.

The mechanical removal system is still just an idea. Being able to protect the CFA from the hazards of drill liquid, would hopefully entice others to investigate the brittle zone more thoroughly. The CFA is a delicate system and the introduction of this removal system could result in new challenges.

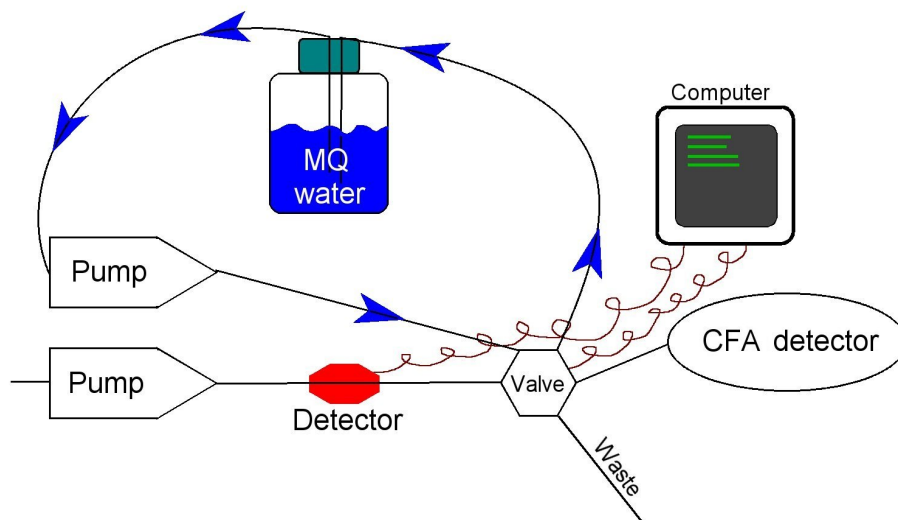


Figure 8.3.1.: One way of removing drill liquid is making a automated system, that derails the drill liquid and send MQ into the CFA when it is detected.

9. Conclusion

The ice from the brittle zone will continue to be a challenge with both pure handling of the ice shards, and the contamination issues from the drill liquid.

But for the CFA, a simple and robust system has been developed that continuously detects and identifies drill liquid contamination in an ice core. Detectable drill liquid is: *D-40/HCFC-141b* used at NGRIP, *Estisol 240/Coasol* used at NEEM and *Estisol 140* that currently is tested for future use. The setup was tested at the NEEM ice core drilling site where it successfully monitored the CFA liquid stream throughout the brittle ice zone. 27 out of 158 measurements proved positive for drill liquid. In the subsequent data analysis the artificial data points caused by the drill liquid were identified. The instruments affected by drill liquid contamination were: the insoluble dust particle, the electrolytic conductivity, the ammonium, the hydrogen peroxide, and the sulfate detectors.

Drill liquid contamination typically happened in the beginning of the measurements while the Milli-Q ice cube was melting on the melt head. As cleaning of the melt head loosens drill liquid residue and the Milli-Q ice cube flushes this, the cube now serves an extra purpose. The Milli-Q water fills the lines with water, and carries any drill liquid residue out of the system before the measurement begins. For this reason the Milli-Q ice cube should be at least 3 cm or longer when working with brittle ice.

The setup tested at NEEM used a deuterium lamp, monitoring the 290 nm wavelength. Potentially, the system can be improved by the use of new powerful LEDs emitting at 240 nm wavelength with better reliability and a longer lifetime than the deuterium halogen light. If applied, it would have to be in conjunction with another LED so the air bubbles also can be detected.

A further development to the CFA system would be to remove the drill liquid from the analytical system before it reaches any sensitive instruments. Such a system could operate either passively (in a detection-warning mode), or could operate actively to ensure that drill liquid does not enter the analytical system.

Given that drill liquid can now be detected, it would be possible to implement a valve which automatically switches at the presence of drill liquid and diverts contaminated melt water away from the CFA instruments, as discussed in chapter 8. The loss of sample resulting from such a mechanism must be balanced against the cost of time, instruments and spare parts required to deal with instrument failures resulting from the contamination of drill liquid.

A more passive system could be used to identify and quantify the amount of drill liquid present in the samples. Such a system could be used in cases where drill fluid coats the inside of the tubing without directly influencing of some detectors, and it would provide the CFA operator with an additional indication of when a full-system maintenance and cleaning is needed.

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A. Appendix

A.1. Break location

Table A.1.: Location of the breaks. measured from the bottom

Bag #	Break (cm)	Break (cm)	Break (cm)	Break (cm)	Break (cm)	Break (cm)	Break (cm)	Break (cm)
1107-1108	0.0	108.0						
1173-1174	N/A							
1177-1178	0.0	12.3	102.2					
1203-1204	0.0	32.2	62.3					
1207-1208	0.0	65.2						
1209-1210	0.0	52.0	69.5	104.2				
1247-1248	N/A							
1281-1284	0.0	16.5	64.4	85.3				
1303-1304	0.0	13.0	23.5	51.4	67.2			
1313-1316	0.0	18.3	41.9	52.6	66.6	81.3	95.9	
1317-1318	0.0	20.6	32.0	50.7				
1329-1332	0.0	15.9	34.4	44.8	56.3	69.7	81.2	110.2
1337-1340	0.0	16.2	31.3	56.9	76.5			
1341-1344	0.0	11.0	26.9	64.2	75.3	92.7		
1349-1350	0.0	54.5	68.7					
1431-1442	0.0	12.0	30.1	48.2	60.8	69.5	102.3	
1915-1998	0.0	11.6	20.6	32.4	44.4	56.4	72.6	84.8
1999-2053	0.0	15.7	25.7	38.2	62.4	76.4	87.4	122.8
2156-2159	0.0	18.0	30.4	38.3	61.0	79.5	100.0	
2206-2209	0.0	57.0	97.7	105.9				
2214-2215	0.0	31.3	44.0	69.0	123.0			
2238-2239	0.0	14.6	28.0	86.5				
2270-2271	0.0	48.8						
2308-2309	0.0	92.7						
2312-2313	0.0	13.9	39.5	55.1	82.5			
2326-2327	0.0	16.9	62.2					
2328-2329	0.0	109.7						

Note: Two cutting sheets were not available, therefore N/A.

A.2. The Matlab scripts

A.2.1. The detector program

The main detector program is a list of all data files collected at NEEM, calling the detector function.

```
% TD(1)= detectorfunction4('2270-2271 no cont.txt',5,1.20);
% TD(2)= detectorfunction4('2308-2309 no cont.txt',6,1.20);
% TD(3)= detectorfunction4('2312-2313 no cont.txt',7,1.20);
```

... and so on and so forth for all the 158 measurements

```
function[TD]=detectorfunction4(filename,j,flow)
D=load (filename);
t=D(:,1); % time in sec
A=D(:,2); %Channel A 290nm
B=D(:,3); %Channel B 435nm

mA=mean(A);
mB=mean(B);
topA=zeros(length(t),1);
topB=zeros(length(t),1);
topC=zeros(length(t),1); % used for calculating drill liquid (DL) amount
top=NaN(length(t),1); % used for plotting
for ii=1:length(t)
    if A(ii) < mA-100
        topA(ii)=1;
    end
    if mB-100 > B(ii) && B(ii) > 1500 % Dill Liquid threshold
        topB(ii)=1;
    end
    if topA(ii) >0 && topB(ii) > 0 % positive DL detection
        top(ii)=1000; % used for plotting DL event
        topC(ii)=1; % used for calculating the DL amount
    end
end

end

%% Amount of Drill liquid in the system
t_avg=t(end)/length(t); %average the length of time per sec
antal=sum(topC); % amount of positive results

drillliquid_ml=(t_avg*antal)/60*flow*(1/7); %[ml] there are 7 lines on the BERN CFA

TD=drillliquid_ml;
```

```

%% plot
xrange=[0 D(end,1)];

figure(j)
plot(t,B,'b', t,A,'r', t,top,'ko',xrange,[0 0],'k-')
legend('435.83nm','290nm','Drill liquid','Location','Best')
title(['Amount of drill liquid = ',num2str(drillliquid_ml), 'ml'])
xlabel('Time in sec')
ylabel('Intensity(counts)')
set(gcf, 'Name', num2str(filename))

```

A.2.2. Processing of the Bern data

```

%% Bern data
%% Load data
clear, clc, close all
tic
display('          Loading NEEM data')
[CFA_Index,Counts,Status,AS_Nr,Time,Cond,Dust,Na,H2O2,HCHO,NO3,...
Ca,NH4,SO4,DOC_1,DOC_2,DOC_3,DOC_PD,NC,pH]...
    =textread('bern\110617-015.NEEM.dat',...
'%f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f %f*[\n]', 'headerlines',4);
toc

%% drill liquid
tic
display('          Computing drill liquid events')
D=load('2308-2309 no cont.txt');
[top,topP,t,A,B]=drilldetector(D);

toc

%% aline the data
delay=-20;
t_Cond=CFA_Index+delay    -187-47 ; % Counts goes up, measures all ions
t_Dust=CFA_Index+delay    -187-40 ; % Conds gets sky high
t_Na=CFA_Index+delay      -250    ; % damage column drill, liquid gets stuck
t_H2O2=CFA_Index+delay    -200-41 ; % ?
t_HCHO=CFA_Index+delay    -300    ; %
t_NO3=CFA_Index+delay     -306    ; % damage column Counts goes up, with a tail,
t_Ca=CFA_Index+delay      -277    ; % ?
t_NH4=CFA_Index+delay     -318+9+50; % ?
t_SO4=CFA_Index+delay     -230-85 ; % damage column drill, liquid gets stuck

```

```
t_pH=CFA_Index+delay      -250      ; % counts goes up, disturbs it some how,

%% work the data

CondI = interp1(t_Cond,Cond,t)*13000;
DustI = interp1(t_Dust,Dust,t)*2000;
NaI = interp1(t_Na,Na,t)*700;
H2O2I = interp1(t_H2O2,H2O2,t)*1000;
HCHOI = interp1(t_HCHO,HCHO,t)*500000;
NO3I = interp1(t_NO3,NO3,t)*800;
CaI = interp1(t_Ca,Ca,t)*9000;
NH4I = interp1(t_NH4,NH4,t)*1000;
SO4I = interp1(t_SO4,SO4,t)*3100;
pHI = interp1(t_pH,pH,t)*10000;

timedelay=-43; % time delay between my detector and the rest of the CFA

xrange=[100 400]; % på subplot
breaks=[0.0 0.0 92.7]; % [cm]
t_break=60; %3 cm MQ ice = 60sec
plotter2(2308,t,top,CondI,DustI,NaI,H2O2I,HCHOI,NO3I,CaI,NH4I,SO4I,pHI,...
A,timedelay,xrange,breaks,t_break)
title('From bag 2308 to 2309, depth 1268,85 to 1296,95 meters')
xlim([0 2000])
```


A.3. IPY Poster

A.4. Manuscript and Co-authorship statement