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**Master 2 Sciences de l'Univers, Environnement, Ecologie
Parcours Hydrologie-Hydrogéologie**

**Caractérisation de l'hiver 2009/2010 par les isotopes
stables de l'eau dans le manteau neigeux en Scandinavie.**

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Abstract

Fresh snow samples were collected in Scandinavia between the latitudes of 59°N and 65°N. The winter of 2009/2010 is characterized by an exceptionally high snow depth in this area and by the lowest NAO (North Atlantic Oscillation) index ever recorded (180 years of recording). This region receives precipitation from both westerly (Atlantic) air masses and from the northeasterly system. I collected 936 samples from about 24 sites spread over about 300 000 square km, from 4th March to 26th March by car. The samples were analyzed for density and the Stable Water Isotopes ($\delta_{O^{18}}$ and δ_D known as SWI). In addition, 128 cores were taken and half of them were layered in order to detect the evolution of SWI signal during the winter season. The huge quantity of samples was analyzed thanks to the new technology Laser Water Isotopes Analyser recently installed in Stockholm University. The results from this new sampling method with a new device require an explanation of the procedure used and the various problems encountered, presented in this study.

A high concentration of core sampling around the 63°N parallel, enables a good resolution of the isotopic signal in the accumulated snowfalls during the winter season. These results show for the first time the westerly air masses effect from the Atlantic according to the samples analyzed. Moreover, the REMOiso model enables us to detect the low NAO index in the SWI signal on this transect and confirms the exceptionality of the phenomenon. The comparison of vertical SWI signal in the snow pack shows the homogeneity of the signal on the same site, and also on a larger scale (100km). The weather datas, at Vindeln, enable to date de different layer of the cores and to give a $\delta_{O^{18}}$ value for each snow event.

Finally, this study is a contribution to recording, commenting on and understanding this very exceptional winter. This work is also a guide for future similar work, which will be done in order to record other winters in the same way. Many applications of this new kind of sampling are of interest to several domains in research, for example the analysis of other elements in the snowpack, the understanding of the atmospheric process, the validation of the outputs of climate-isotopic models or inputs in hydrologic-isotopic models, and they will further the understanding of the SWI proxy in paleo-climatology.

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[CHARACTERIZATION OF THE
WINTER 2009/2010 BY THE STABLE
WATER ISOTOPES IN THE SNOW
PACK OVER SWEDEN]

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Finally, I thank with all my heart the people who have encouraged me in my first work experience in another country, my family, my friends and my teachers.

I. Introduction

A. Outline of the Present Study

This study will present the work achieved during an internship in the Geochemistry Department of Stockholm University between February and September 2010. This thesis was supervised by Christophe STURM who is a model programmer (modelisator) in the Geochemistry Department.

Overall, this work consists of taking advantage of the abundance of undisturbed snowpack in the north of Sweden, in order to carry out a field campaign to collect snow cores in Sweden and to analyze them for the $\delta_{O^{18}}$ and the δ_D . Moreover, this exceptional winter is characterized by a very high snow depth in the studied area, and globally the lowest negative NAO (North Atlantic Oscillation) index for the winter season ever measured in 180 years of records. Thus, this study offers the possibility of recording, commenting on and discussing the unusual winter of 2009/2010.

The scientific questions which motivated this endeavour were three : How far can we record and comment on the winter using the $\delta_{O^{18}}$ and the δ_D signal of snow cores over Sweden? Can we detect the NAO index in the SWI signal in the snowpack in Sweden? What are the limits of and the repeatability of this method?

As this kind of field trip has not been made before, this study will detail the strategy and the method of sampling. moreover, throughout this study, the laboratory used for the first time a new method of SWI measure by the LWIA which needs to be parameterized and calibrated. That is why we will also detail this important part of the work in order to appreciate errors of analysis at source and quantify them. Finally, the mass of data will be interpreted, in order to attempt answers to the questions which gave rise to this study.

B. General Context of this Study

1. The new technology Laser Water Isotope Analyser (LWIA)

In the past few decades, hydrogen and/or oxygen isotopes have been utilized in studies of different environments to address several areas of research. The conventional method used to determine the $\delta_{O^{18}}$ and the δ_D in water samples is mass spectrometry. The disadvantages of this methodology are the time- and labour-intensive measurements, coupled with the high equipment and operational costs. Recently, alternative instruments for isotopic analyses have been developed to offer more cost-effective opportunities for the determination of stable isotope ratios in the vapour or liquid water phase. This is the Laser Water Isotope Analyser.

2. The Project

This study is part of a larger project led by C. STURM which needs knowledge in climatology, hydrology, lake sediments interpretation. It is important to understand the aim of this project.

The Stable Water Isotopes (called SWI, which are usually the Oxygen 18 and the Deuterium) are widely used as a proxy to well understand past climatic change, and to enable us to forecast our future climate. SWI can be measured in a wide range of paleo-archive materials (e.g. ice cores, lake sediments, tree cellulose, speleothems), but the physical interpretation of their isotopic signal remains controversial. This controversy often springs from the simple analysis of this core using the first parameter determining the amount of the SWI which is the temperature (Dansgaard, 1964), and presuming that the climate dynamic was unchanged. Nevertheless, there are a large number of parameters which can play a role

in the amount of SWI in the water. The last concrete example is the case of Greenland ice-cores interpretation, which underestimates the mean annual temperature: scientists considered that the dynamic of the atmosphere was non-modified, but the air mass was in reality from another origin, which changed radically the amount of Oxygen 18, but not necessarily the average temperature. If we have succeeded in identifying this error, it is still by no means certain that we have not erred in our interpretation of the lake sediments core, since we know we must also consider the atmospheric circulation and the hydraulic dynamics, which can be very different from one catchment to another.

Atmospheric circulation and hydrology models offer the opportunity to simulate fractionation process at each phase change. Thereby, the influence of temperature but also synoptic circulation on the $\delta^{18}\text{O}$ signal is explicitly reproduced in the model. The goal of the ARTEMIS project is to use these integrating $\delta^{18}\text{O}$ models and combine them in order to achieve the best interpretation of the climate proxies.

This project needs a great deal of inter-disciplinary application, and that is why I was encouraged to use my knowledge of hydrology and especially of the SWI. Using the snow core to characterize the $\delta^{18}\text{O}$ in the precipitation will be very useful for this project for several reasons. Firstly, it will be possible to compare the $\delta^{18}\text{O}$ atmospheric model output with the signal in the cores, secondly, we can introduce the SWI in the hydrology models, and finally, as a large quantity of samples has not previously been analyzed, it will be possible to achieve a sound interpretation of this year in order to understand the isotope signal related to the climate circulation.

II. Review of literature

A. The water stable isotopes in the precipitation

This chapter aims to synthesize the understanding of the isotopic signal in the precipitation, as we use it in this thesis. The most frequently cited reference to characterize this phenomenon is Dansgaard, 1964. (Dansgaard 1964). Thus, we will summarize the information from this paper, and add update reference largely drawn from the last IAEA reference (Mook, et al. 2001). This is a review of basic theoretical concepts and principles of isotopes hydrology methodologies and their practical applications. Readers may wish to refer to (Mook, et al. 2001), chapter II : atmospheric water, for more information and references about stable isotopes.

1. General water stable isotopes knowledge

a) Notation

There are 2 elements (H and O¹⁶) in the water (H₂O) which have an abundance of more than 99% and the two measured rare stable isotopes of H and O are respectively D(H²) (Abundance = 0,015 %) and O¹⁸ (Abundance=0,2%). Then there are 6 combinations possible of water stable isotopes in the water, H₂O¹⁶, HDO¹⁶, H₂O¹⁸, D₂O¹⁶, HDO¹⁸ and D₂O¹⁸. We do not consider the three last combinations, because the quantity is infinitesimal compared with the abundance of HDO¹⁶ and H₂O¹⁸ in the water. Thus, when we are doing isotope analysis of the water we measure the quantity HDO¹⁶ and H₂O¹⁸. As the quantity of stable isotopes in the water is very low we introduce the δ notation, which may be considered as

$$\delta_D = \frac{\left(\frac{\text{HDO}^{16}}{\text{H}_2\text{O}}\right)_{\text{sample}} - \left(\frac{\text{HDO}^{16}}{\text{H}_2\text{O}}\right)_{\text{standard}}}{\left(\frac{\text{HDO}^{16}}{\text{H}_2\text{O}}\right)_{\text{standard}}} * 10^3 \text{ ‰} \quad \delta_{O^{18}} = \frac{\left(\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}}\right)_{\text{sample}} - \left(\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}}\right)_{\text{standard}}}{\left(\frac{\text{H}_2\text{O}^{18}}{\text{H}_2\text{O}}\right)_{\text{standard}}} * 10^3 \text{ ‰}$$

Equation 1 definition of δ_D and $\delta_{O^{18}}$

During the sixties, a reference standard was established, to allow the comparison between research programs which is SMOW (Standard Mean Ocean Water,(Craig, Standard for reporting concentrations of deuterium and Oxygen-18 in natural water 1961)). It is defined as $\delta_{D,SMOW} = 0\text{‰}$ and $\delta_{O^{18},SMOW} = 0\text{‰}$.

b) Isotope fractionation factors

The isotopic composition of natural waters covers a large range, which amounts to more than 400‰ for δ_D and 40 ‰ for $\delta_{O^{18}}$. To explain this difference, the principle of fractionation has to be present.

According to classical chemistry, the chemical characteristics of isotopes are equal. To a large extent this is true. However, if we measure the δ_D and $\delta_{O^{18}}$, we realize that there is a difference between the water which comes from different places (around 0‰ for the sea water and -40‰ in term of $\delta_{O^{18}}$). Indeed, tiny differences exist between the isotopes which react differently to a transformation. The phenomenon is called the "isotopic fractionation" and is responsible for this variability. Physically, for the water, the fractionation is due to the fact that the heavier molecules have a lower mobility. The kinetic energy of a molecule is solely determined by temperature $kT = 1/2 mv^2$ (k = Boltzman constant, T = absolute temperature, m= molecular mass, v = average molecular velocity). Therefore, molecules have

the same $1/2 mv^2$, regardless of their isotope content. This means that the molecules with larger m necessarily have a smaller v . The consequences for the water are that HDO^{16} and H_2O^{18} have a lower velocity and therefore a lower vapour pressure than H_2O ; they also evaporate less easily.

This physical process explains why the vapor is depleted in Oxygen 18 and Deuterium in comparison with the ocean water. Moreover, during a rain event the same process is applicable to the vapor, and the heavier molecules will condense more easily. The further the clouds go far from the origin of the evaporated water, the more the cloud will be depleted in Oxygen 18 (depending also of the amount of rainfall during the airmass transportation). This process is called the Rayleigh distillation (Figure 1).

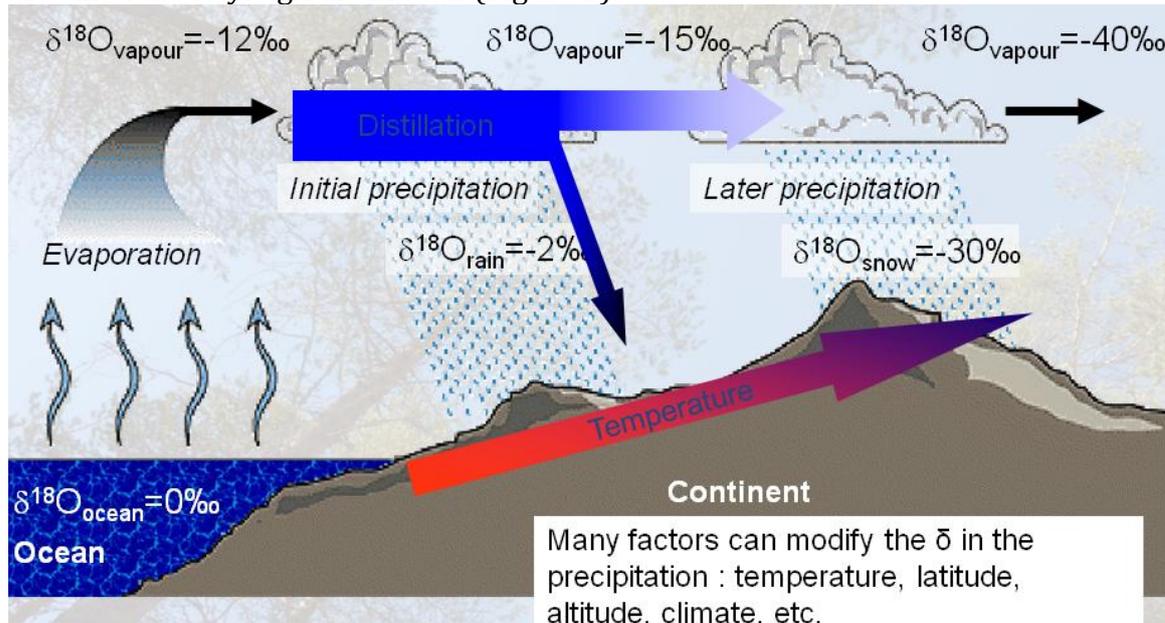


Figure 1 Stable isotope and the water cycle. The Rayleigh distillation in the nature

B. The snowpack: a recording of the past snow event

According to different studies, if the snowpack is not disturbed, i.e. the temperature doesn't exceed $0^{\circ}C$ during the snowpack formation, the isotopic signal in the winter precipitation (snow falls) is conserved in the snow pack. Several studies used this finding. Here are two of them. Firstly, (RODHE 1987) made a comparison between $\delta_{O^{18}}$ of the snow pack and the $\delta_{O^{18}}$ of winter precipitation (Figure 2) and showed that a good relation exists between these two variations, if we are speaking in terms of water equivalent. Each part of the snow core represents so to speak a smoothing out of the different snow event collected. This work was undertaken in order to determine the "Origin of the stream water". Secondly, the same idea was used by (SINCLAIR et MARSHAL 2008), in order to analyze the "Post-depositional modification of stable water isotopes in winter snowpack in the Canadian Rocky Mountains". Each core site was sampled several times during the winter season in order to detect the evolution of the snowpack in terms of SWI (Figure 3).

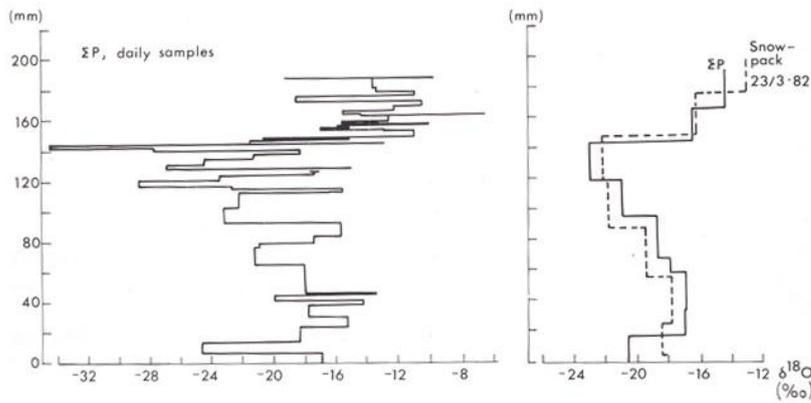


Figure 2 $\delta_{18}\text{O}$ layering of the snowpack compared to the $\delta_{18}\text{O}$ of winter precipitation. Vertical axes: water equivalent of precipitation or snowpack. Svartberget 1982 (RODHE 1987)

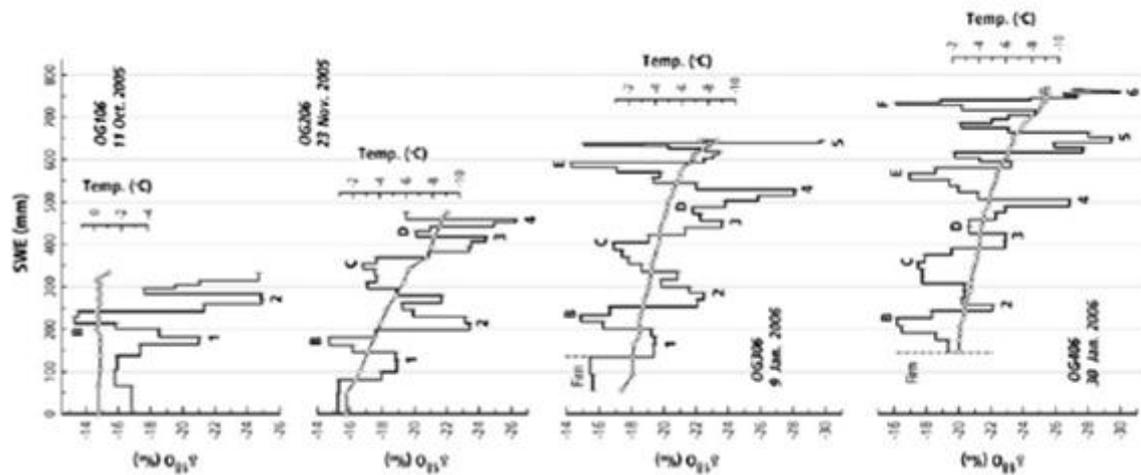


Figure 3 $\delta_{18}\text{O}$ stratigraphies and temperature profiles of snowpits in the same site from the 2005/06 accumulation season by (SINCLAIR et MARSHAL 2008).

III. The site description

A. Geography

The investigation was performed mostly in Sweden between the latitude 59°N and 65°N, ie. between Umeå/Vilhelmina and Stockholm which are separated by 550km. The Sweden between these latitudes presents the particularity to have a regular section est-west from the north to the south with the Baltic sea to the west and the the Scandinavian mountain chain (Skanderna) to the east which determine the boundary between the Sweden and the Norway. The highest point in this Swedish relief is [Kebnekaise](#) at 2,111 m (6,926 ft) above sea level. And the average altitudinal gradient est-west between the sea and the mountain is 0,0023 m/m (if we consider the average of the level of the average of altitude est-west of the chain as 700m and the distance between the mountain as 300km). This symetrie has been a criterion to determine the sites to do the field trip. This area encountered characteristic types of landscape encountered in Sweden, with Gneiss or granit rock covered by glacial till soils, vegetated by coniferous forest (mainly spruce or pine forest).

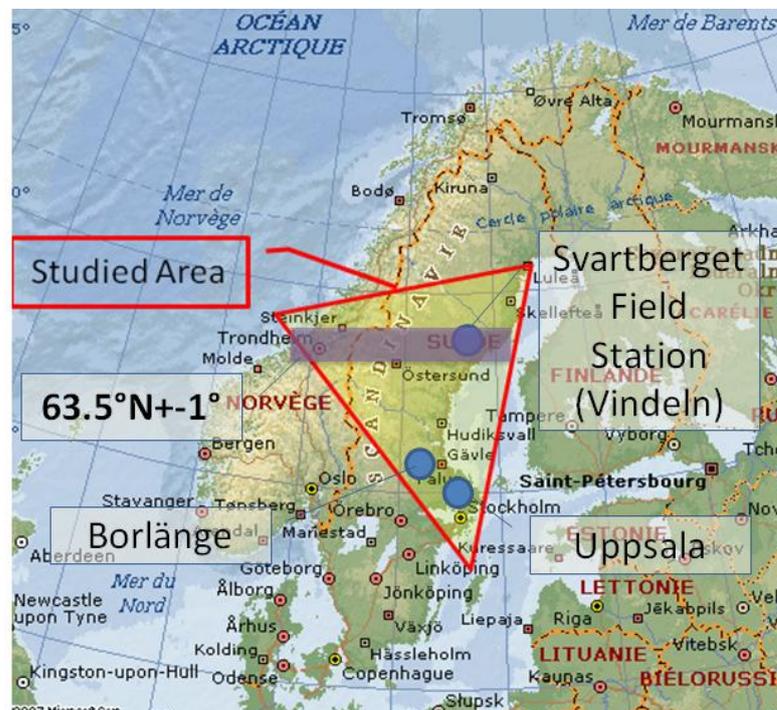


Figure 4 Location of the studied area in Scandinavia (source : Microsoft Map point)

B. Climate

The climate in this part of Sweden is defined as the humid continental climate which is marked by variable weather patterns and a large seasonal temperature variance. In winter, the precipitation in this part of Sweden are mostly snow falls and in summer the temperature are higher than the normal in temperature for the same latitude, mainly because of the Gulf Stream. An other parameter can be identified as a determination of the climate in Sweden during the winter. This is the North Atlantic Oscillation (NAO).

The North Atlantic Oscillation (NAO) can be regarded as the changes in the difference in atmospheric pressure between the Azores and Iceland. This climatic oscillation has a strong influence on the regime of the westerly winds across the North Atlantic resulting in changes in

winter temperatures on both sides of the Atlantic The NAO plays an important role in circulation and convection in the North Atlantic (Figure 6)

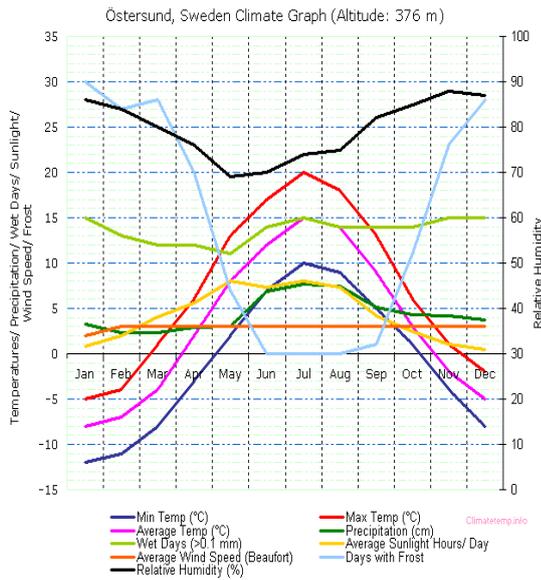


Figure 5 Weather condition in Östersund (nearly the center of the studied area) (source : clamatemp.info)

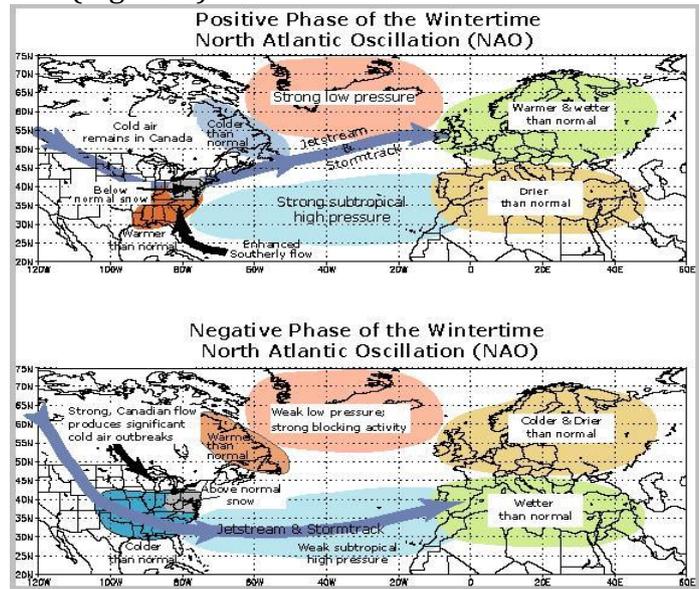


Figure 6 Positive and negative phase of the wintertime North Atlantic Oscillation (source : NOAA, Lamont-Doherty Earth Observatory)

C. Remo-iso outputs : the stable water isotopes signal in the precipitation

REMO_{iso} (K. Sturm June 2005., K. B. Sturm 2005) builds on the REgional MOdel REMO v5.0, with embedded module for stable water isotopes δ_D and δ_{O18} . REMO_{iso} uses (almost) identical physical parametrizations to the global circulation model ECHAM (European Climate Hamburg Model) v4.5. Its standard resolution is 0.5°, approx. 50 km.

Run this model on the Scandinavia thanks to give different spatial repartition of the SWI signal in the precipitation in the past years. For the Scandinavia it was possible to run this model between the years 1959 and 1999 with a resolution of 50 km . This resolution is enough comparing to the resolution of our field campaign (approx. 50km). Therefore, it will be possible to compare the outputs from REMOiso from December January and February (DJF) with our results which frame this period. This comparison is very important to prove the detection of the very low NAO index.

That's why, we did a selection of the most NAO negative years (NAO-) and the most NAO positive years (NAO+) between 1959 and 1999. This selection is done in order to determinate the difference, in term of Oxygen 18 in the precipitation, between this two different climates dynamic in winter (Figure 7). Moreover the average direction of the wind in DJF is plotted on the maps to understand the dynamic of the SWI signal in the precipitation. The last map presents the difference between NAO+ and NAO- calculated maps. This difference indicates that during the most negative NAO years the composition of the precipitation is more depleted in Oxygen 18 (roughly 1‰). Furthermore the location where the difference is the most noticeable (more than 2‰ of difference) is in our studied area in the north. This is precisely in this region that the comparison will be done in VI.A.5. **A mark of the very negativ NAO index in the snow pack.**

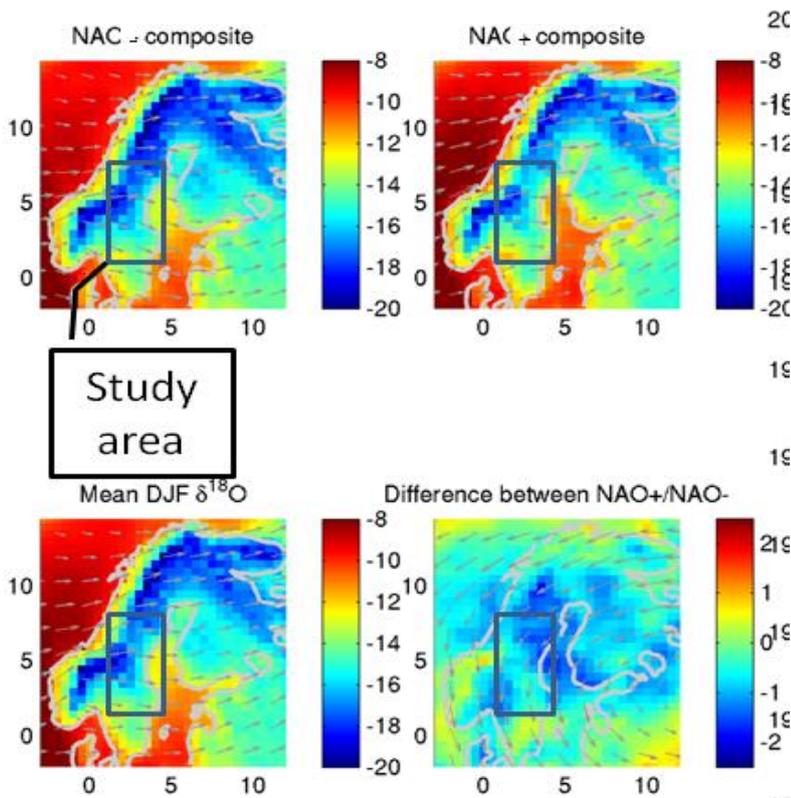


Figure 7 REMO-ISO model outputs : wind direction and Oxygen 18 in the precipitation.

Bottom left : Oxygen 18 spatial variation average for the months December January February (DJF) on 40 years (1959-1999).

Top left : Oxygen 18 spatial variation average for the 15 years most NAO negative during the 40 years of recording.

Top right : Oxygen 18 spatial variation average for the 15 years most NAO positive during the 40 years of recording.

Bottom right : Difference between the NAO+ years and the NAO- years, this figure shows the influence of the NAO on the wind direction and the Oxygen 18 composition in the precipitation.

D. The winter 2009/2010 in the studied area

1. Snow depth and temperature

The winter (December 2009 to March 2010) is characterized, for the studied area by an unusual snowfall amount coupled by very low temperature. Indeed, the usual snow depth around the 15 March for our studied area range between 10 and 50 cm with 30% chance to have no snow in Stockholm (Figure 10).

This year (2009/2010), snow depth records were measured close to Stockholm with a maximum over 75cm near Norrköping. The low temperatures, which exceed rarely 0°C (Figure 8), are also advantage to keep the snowpack non-mixed in term of isotopic composition. Thus, all the conditions were luckily unified to carry out this project and collect non disturbed snow cores.

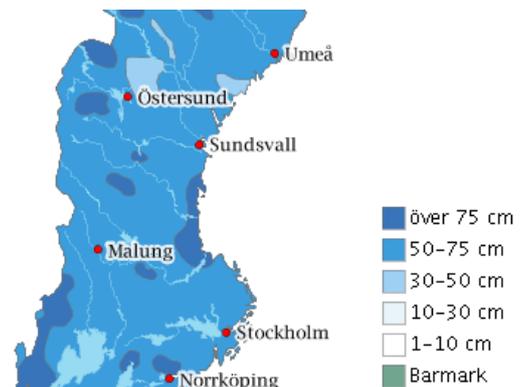


Figure 9 Snowdepth over the studied area (source: SMHI.se) for the end of February.

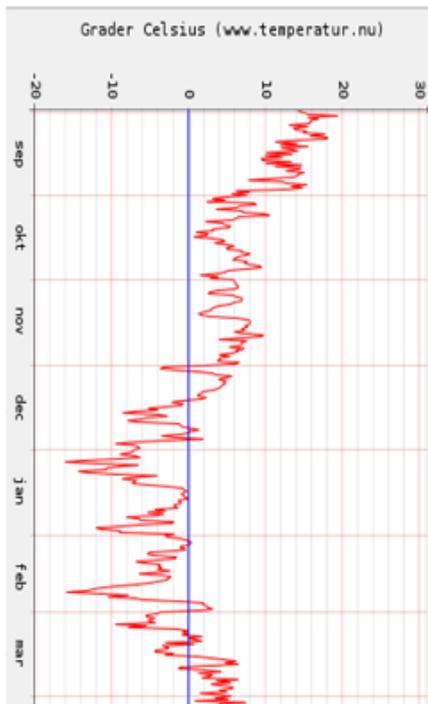


Figure 8 Evolution of the temperature in Stockholm (the most southerly place in the field area) during the 2009/2010 winter season. The temperature exceeded rarely the 0°C. (source temperatur.nu)

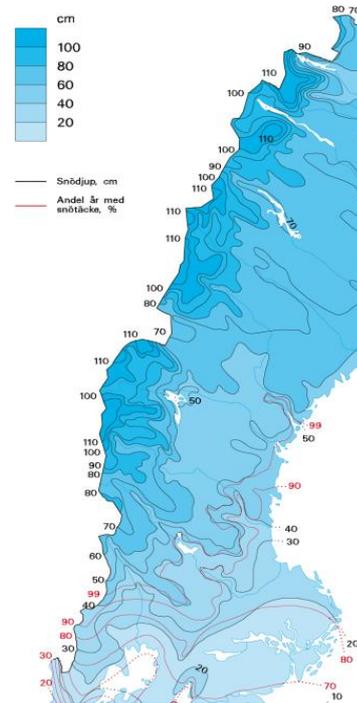


Figure 10 Normal snow depth for the 15th March build from a dataset of snow depth recording on the period 1961-1990. The red line represents the probabilities to have still a snowpack the 15th March.

2. Very negative North Atlantic Oscillation

Although the NAO occurs in all seasons, it is during winter that it is particularly dominant, and therefore the focus of this information sheet is on the December to March period. According to last update of the NAO index for winter time, the year 2010 is the lowest index never recorded before. As the sampling is done during the winter time it is interesting to understand the SWI pattern record for the winter time in our studied area with other years to see this very NAO negative signature.

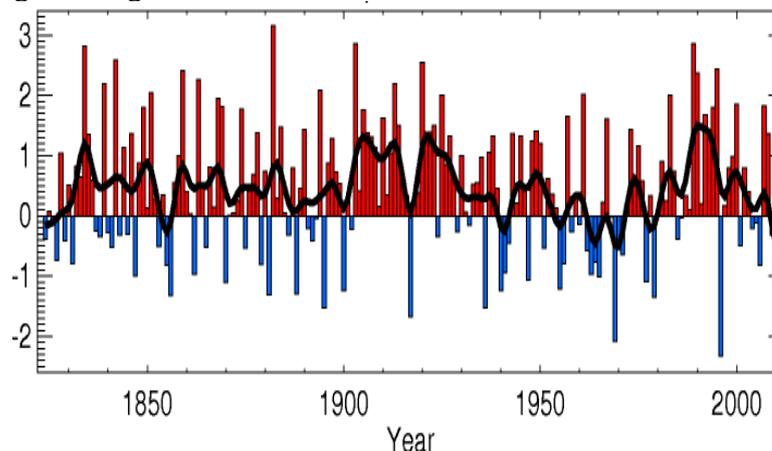


Figure 11 Index of the boreal winter (December-March) mean NAO constructed as the difference in sea level pressure between Lisbon, Portugal and Stykkisholmur/Reykjavik, Iceland from 1864 through 2010. The mean winter sea level pressure data at each station were normalized by division of each seasonal pressure by the long-term mean (1864-1983) standard deviation. The heavy solid line represents the index smoothed to remove fluctuations with periods less than 4 years. The indicated year corresponds to the January of the winter season (e.g., 1990 is the winter of 1989/1990).

IV. Field trip

A. Method of determination of the sample sites

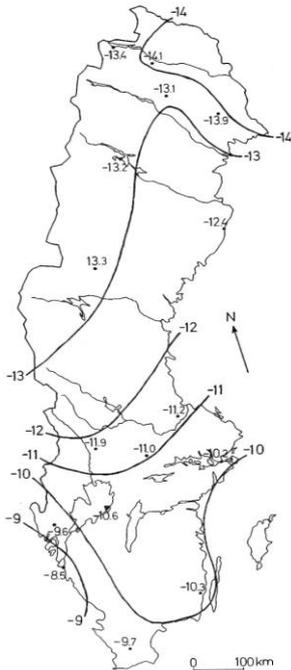


Figure 12 Mean δ_{18O} values and isoline pattern according to 5 years of sampling (1975-1980) by (Burgman, et al. Dec 1981)

The objective of the field campaign was to collect the maximum of snow core in few days. This condition was due to the homogeneity of the results. Also the field campaign was planned to be realized in the middle of march (between the 16th and the 26th). During this period the snow is still unmelted and there is almost no more snowfall. Then it's the perfect time to have the best recording of the winter season thanks to the snowfall.

A strategy to determine the sites was lead before the field trip. First, we considered the variability of the Stable Water Isotopes in Sweden thanks to (Burgman, et al. Dec 1981) and the outputs of the Remo-iso model (Figure 7). The variability is roughly 1 ‰ per 100km for the $\delta_{O^{18}}$ (Figure 12). Secondly, is interesting to realize the samplings close to the different sites already studied ((RODHE 1987, Burgman, et al. Dec 1981). Finally, we did the sampling close to the weather stations which measure the temperature, the precipitation (snow and rain) and the snow depth in continue by the SMHI.

B. Method of sampling

The field campain was realized by car to carry the equipment and the samples.

To sample the snow we used a Russian corer. This tool is normally used for the lake sediments but it appears also very practical for the snow. Indeed, it's the best that we found to have a non disturbed core of snow, especially for the fresh snow on the top layer. This tool gives a core with a demi circle section and was limited to 1,5m high (less than the highest snowpack we found).

For each sites, we plan to do 4 or 6 cores: one with a high resolution of 2.5cm with a total core very close to give an average value of the winter season for the isotopes, one or two replicates with a 5 cm resolution to validate the results of the 2.5 cm core (generally the first replicate were about few meters from the 2.5 cm core and the second replicate were at few kilometres). The aim of the replicates confirm the results of the 2.5cm cores of the replicates confirm the results of the 2.5cm core.

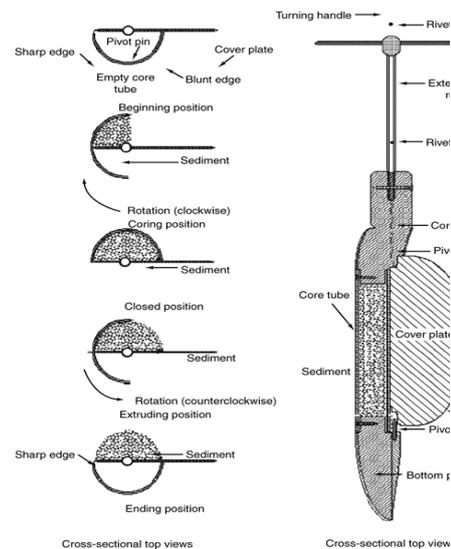


Figure 13 The Russian corer : commonly used to collect the sediments this tool was used in this study to collect the snow samples

The high resolution of 2.5cm was chosen because it was technically easy to reach and it was never used according to the studies we read (RODHE 1987, SINCLAIR et MARSHALL, Temperature and vapour-trajectory controls on the stable-isotope signal in Canadian Rocky Mountain snowpack 2009). To cut the snow cores with the different resolutions we used a trowel and to give the position we used a GPS. Each cores were described separate and measure the different layer and describe the state of the snow in this layers (fresh snow, compact snow, depth hoar, ice crust, etc.). For each stratigraphied snow core a picture was taken to record the aspect of the core and moreover another picture of the environment around the point of sampling was taken to help the post analysis (tree, size of the open field area, etc.).

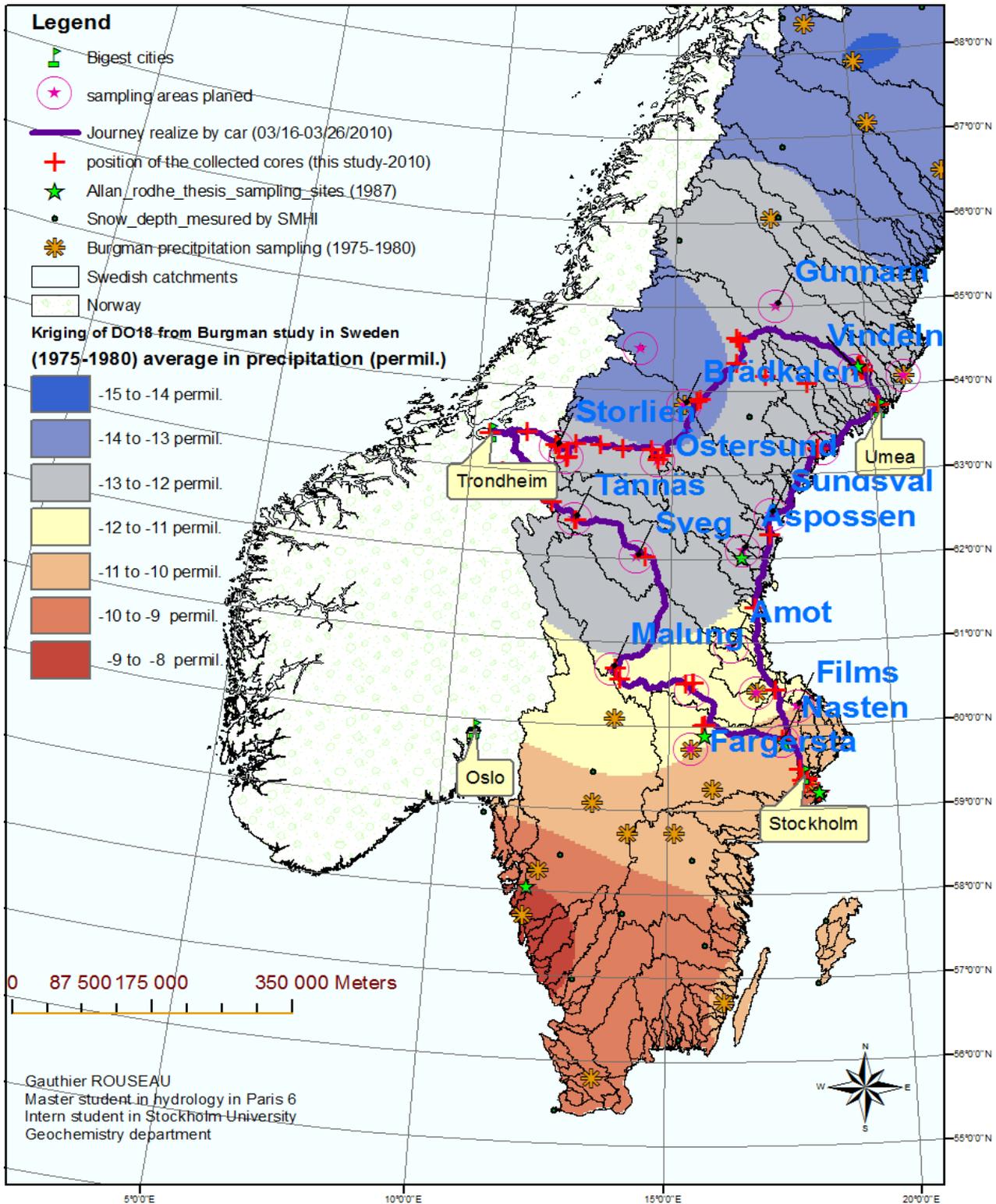


Figure 14 View of the different sites studied in the past (Bergman, 1980, Allan Rodhe, 1987). Position of the weather stations which measure the snow depth. Areas of sampling planned before the field trip with the name of the different places in blue. Position of samplings realized (the red crosses). The background of this map represent the average of the Oxygen 18 between 1975 and 1980 thanks to a krieging build from the Burgman data aver Sweden(Burgman, et al. Dec 1981).



Figure 15 View of the different tools used for the sampling



Figure 16 View of the sampling area
(one picture is taken for each site)



Figure 17 picture of the core with
the scale in order to describe it

Because of the field work some sites were not sampled exactly with the protocol i.e. as we must do this analysis by car during 10 days and drive 3000 km it was sometime impossible to carry out exactly this protocol. Then sometimes, because the depth was too high it was impossible to do on time the 2.5cm resolution and we did only 5cm resolution [Table 1]. We also did a high geographical resolution in the Jämtland region because a lot of studies were run in this area and in Vindeln close to Umea because this area is very well studied.

Finally, 936 snow samples from 63 cores were collected from 24 sites in the north of Sweden. Snow samples were bagged hermetically and transported to Stockholm University – Geochemistry Department by car. They were melted during the transportation and in the cold room in the department. Then, they were bottled for the isotope analysis (10ml for each sample). Analyses were conducted by the laser spectrometer which is the subject of the next part.

Name of the site	Date of sampling	Number of replicates	Number of 2.5 cm resolution core	Number of 5cm resolution core	Number of 'total' cores	Latitude	Longitude
Stockholm	3-14/3	8	6	0	7	59,1	18,1
Uppsala	16/3	3	1	2	3	59,8	17,6
Fargersta	16/3	3	1	2	3	59,7	15,5
Borlänge	17/3	3	1	2	3	60,4	15,5
Malung	17/3	3	1	2	3	60,7	13,7
Orsa	18/3	1	0	0	1	61,1	14,6
Sveg	18/3	1	1	0	1	62,0	14,2
Tännäs	19/3	3	1	2	3	62,5	12,7
Trondheim direction 1	19/3	1	0	1	1	62,6	12,1
Trondheim direction 2	19/3	1	0	1	1	63,0	10,8
Trondheim	20/3	1	0	1	1	63,4	10,4
Trondheim--Storlien	20/3	1	1	0	1	63,5	11,4
Storlien-Stur-Ulvan (Jamtland)	20/3	5	2	2	5	63,2	12,4
Are	21/3	2	0	2	2	63,3	13,8
Östersund	21/3	3	2	1	3	63,2	14,6
Breckälen-Strömsund	21/3	3	1	1	2	63,2	14,6
Vilhelmina	22/3	2	0	2	2	63,8	15,3
Umea Direction	22/3	2	0	1	2	64,1	18,4
Vindeln	23-24/3	13	7	6	13	64,2	19,7
Umea	25/3	1	0	0	1	63,8	20,2
Ornsköldsvik	25/3	1	0	1	1	63,3	18,7
Sundsvall	25/3	1	0	1	1	62,5	17,4
Direction Stockholm 1	25/3	1	0	0	1	60,4	17,4
Direction Stockholm 2	25/3	1	0	0	1	60,4	17,4
Total	10 days of field trip	63	25	30	62		

Table 1 Overview of the different sites with the type and the number of cores collected during the field trip

V. Material and method for the isotopic analyses

An important part of my work during this internship was to calibrate the LWIA. Indeed, it was the first time that this laboratory machine was used and it was very important for the department and for this study to have the best results that we could expect with this instrument.

In order to help the future users of this machine we will enumerate the different problems we met and how to solve it (with the configuration of the instrument and the post treatment). Thus, the different attempts to solve the problems will be shown even if they are not always successful to avoid some useless future work. Finally, the precision of our analysis the hypothetical precision that we could reach will be estimate.

A. The liquid water isotope analyzer

All isotopic analyses were conducted using the off-axis integrated cavity output spectroscopy method with a liquid water isotope analyzers (LWIA), model DLT-100, which included three units version 908-0008 and one upgraded version 908-0008-2000 manufactured by Los Gatos Research Inc. (LGR, Mountain View, California, USA).

Off-axis integrated cavity output spectroscopy (OA-ICOS) exploits Beer-Lambert's law to relate the absorption of a laser light passing through a vaporized water sample to the isotopic composition of the sample. Therefore, OA-ICOS instruments allow for the

simultaneous analysis of δ_D and $\delta_{O^{18}}$ for each injection of water, reducing time and operational expenses per measured sample. In addition, simultaneous measurements exclude the potential relative error of two separate measurements of hydrogen and oxygen isotopes at different times. Further advantages include the reduced sample size (1–1.5 ml), easier maintenance requirements without extensive sample pre-processing, shorter time to produce reportable data, and the opportunity for in situ measurements in the field.

The autoinjector was provided with a 1.2 μ l syringe (model 26P/-mm/AS, 7701.2 N CTC) manufactured by Hamilton Company (Reno, Nevada, USA) for the injection of water samples into a heated port. All water samples and working standards were injected into ND8 32·11.6mm screw neck 1.5 ml vials with PTFE/silicone/PTFE septums. The vials were filled with 1 ml of water and placed into 54 position trays on the auto-injector tray holder. According to the manufacturer's specifications (Los Gatos Research Inc., 2008), the DLT-100 908-0008 LWIA provides isotopic measurements with a 1- σ precision below 0.6‰ for δ_D and 0.2‰ for $\delta_{O^{18}}$.

B. The error factors

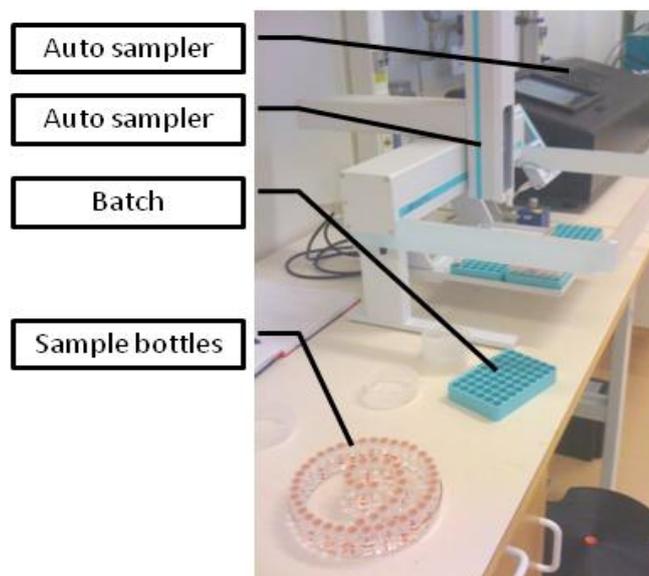


Figure 18 The laser spectrometer for the water stable isopes analyse

The builders of this instrument didn't give the procedure to analyze the samples. So it was my role to determine the best procedure. There were several parameters to determine: the number of injections per samples, the number of standards, the number of sample analysis between each standards analysis. That's why it was very important to well understand the different problems and set the parameters in order to minimize the error.

1. The memory effect

In two consecutive injections, the first injection has a non-negligible effect on the next one. Indeed, the needle is not washed and clean, and there are still micro droplets, which are mixed with the new injection. Then, to execute the analysis of one sample you need to do several injections: the first ones are not taken into consideration (because they are polluted) instead of the last ones which are the only ones valid (non polluted). The number of injection is not fixed and you need to determine the best configuration.

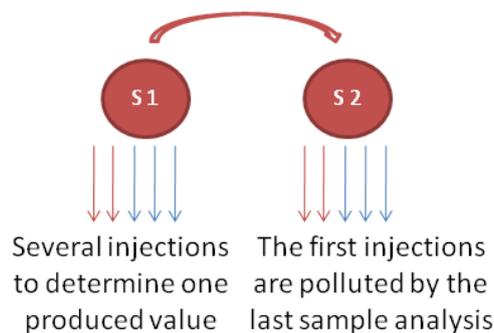


Figure 19 Diagram to illustrate the pollution of the first injections by droplets

2. The pollution of the standards

As some droplets are carried by the needle and as the needle is in contact with the standards, when one configuration of standards is used several times, they will be polluted. Then the δ_D and the δ_{O18} will be modified. To avoid this problem, you can use instead of one bottle for one standard, two bottles for one standard, which are analyzed consecutively. We detail this method in (V.D).

3. The gap effect

The machine doesn't give directly the value but a value with a gap between the real value and the value given by the machine. The value given by the machine depends on the industrial adjustment of the instrument. To determine this gap, standards must be used in order to quantify this difference. The standards are samples having the exactly known values of δ_D and δ_{O18} . As the gap can be different if you have a big value or low value, you need minimum two standards to define the "a" and the "b".

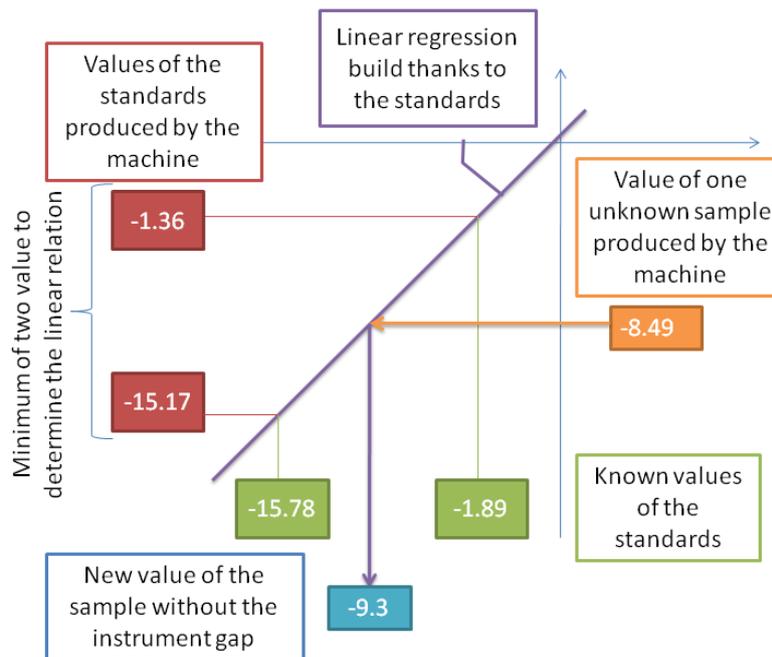


Figure 20 Diagram to show how to proceed to determine the gap

4. The instability of the gap

It appeared that the gap wasn't stable during a sequence of about 12 hours. That means if the gap is determined in the beginning of the sequence and if the correction is set for all the sequence, you will have an error in last sample.

5. The accuracy

As all the instruments, this one presents an accuracy that can be defined by a Gaussian distribution.

6. The duration of the injections

One injection runs roughly two minutes. Then if you want to analyze 50 samples with 12 injections per samples and if you analyze three standards each two samples, you need $(12 \cdot 3 \cdot 25 + 12 \cdot 50) \cdot 2 = 3500 \text{ min} = 58 \text{ hours}$. As we have 950 samples to analyze and the time was limited, it was impossible to conserve this type of parameters so we decided to do only 6 injections and to analyze the standards each 5 samples. With this configuration, it takes 14 hours to analyze 50 samples.

C. Illustrations

1. The problems

To illustrate the instability of the gap, the memory effect and the accuracy effect, we analyzed one standard $\delta_{O^{18}} = -15.55\text{‰}$ 10 times during one sequence with 6 injections. This sample is analyzed each 9 samples analysis and after another standard $\delta_{O^{18}} = -19.57\text{‰}$.

There is a gap because the theoretical value of -15.55‰ is never reached and this gap has a minimum of roughly 0.5‰ . Moreover it is unstable and the maximum is roughly 1‰ . The memory effect is visible and has the same evolution because the previous sample analyses are systematically the same. This sample gives the same amount of droplets which pollute the first injections. This effect is visible for the two first injections.

With this evolution of the analysis, it appears that the evolution looks like an exponential variation which reaches a fix value.

Moreover this figure shows that the variation of the gap between each standard analysis is not negligible (0.5 permil.) and that can compromise the final results. Indeed if we define a gap in the beginning and if this gap is modify after 5 samples analysis, we will have a higher error.

2. The memory effect

As the evolutions looked similar the different evolutions were centered in order to detect a common evolution and quantify the accuracy (Figure 21). The data-set in extract from 5 bathch. Thus 50 analyse with 6 injections were analyzed in order to do statistical analysis. The descriptive statistics were plotted in order to describe the evolution.

This statistical analysis shows that the accuracy effect is similar for all the 6 injection. The standard deviation of the accuracy is about $\pm 0.0733\%$ for the $\delta_{O^{18}}$. The pollution appears to be present until the third injection. the interval between the average expectancy on the 4 last injection and the theoritical value is 0.004 permil this interval is due to the memory effect. Nevertheless, This value is less than the variance of normal distribution on the last 4 injections ($0.0733/4=0.0183$) and can be negligible. Thus, use the average on the 4 last injections (including the 3rd polluted injection) for each analysis will give a result more close to the real value than do average on the 3 last injections.

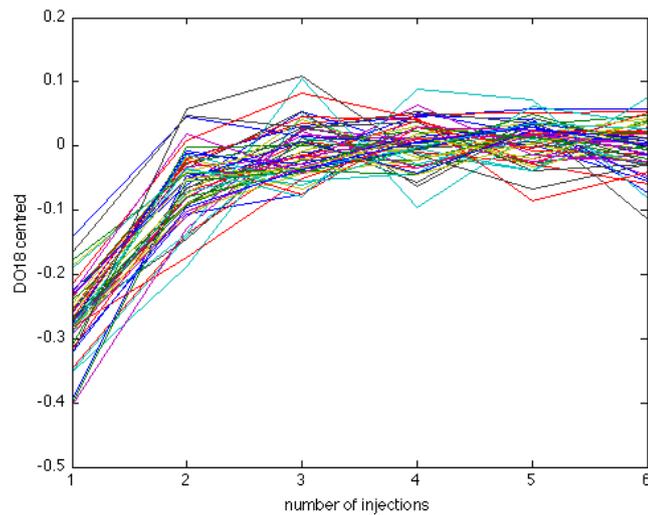


Figure 21 Evolution of the $\delta_{O^{18}}$ value of the same standard LG2 analyse 50 times from several batch. All the evolution are centered on the average of the last 4 injections. The evolutions look similar because the same standard (LG1) is analyzed before the analysis.

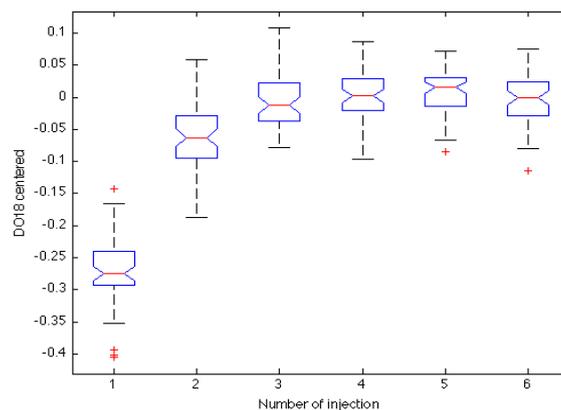


Figure 22 Descriptive statistic of all the $\delta_{O^{18}}$ value (see figure 12) for each injection (red line means mean, the blue means 50 frame the 50 % of the values. the black line up and down means the max. and the min. value.

D. About our analysis

As we realized the problems during the analysis of the 936 samples, we didn't use the same protocol for all the analysis. Then the first protocol that we used was with 5 standards given by the Los Gatos Research (the builder of the laser spectrometer). This standards were calibrated in relation to Vienna Standard Mean Ocean Water (V-SMOW) : LG1: $\delta_{O18} = -19.57\text{‰}$ $\delta_D = -154.1\text{‰}$; LG2: $\delta_{O18} = -15.55\text{‰}$ $\delta_D = -117\text{‰}$; LG3: $\delta_{O18} = -11.54\text{‰}$ $\delta_D = -79\text{‰}$; LG4: $\delta_{O18} = -7.14\text{‰}$ $\delta_D = -43.6\text{‰}$ and LG5: $\delta_D = -2.96\text{‰}$ $\delta_{O18} = -9.8\text{‰}$). We used this protocol for the 532 first samples (Figure 23). When we realized that the standards were slowly polluted by the droplets (see **Error! Reference source not found.**) we decided to change the protocol. Instead of one bottle of standard we put 2 bottle of standard which are analyzed consecutively. This configuration avoids the pollution of the second bottle and with this bottle we could define properly the gap. The first bottles is as a garbage to wash the needles and give new droplets with almost no difference with the second standard bottle. The default of this method is you need twice as much time to analyze the standards because you can't program in detail the procedure with the LWIA (the number of injection is fixed in the beginning of the sequence for all the sample analysis even if you need more or less injections for some of them)

Moreover we realize with the calculation that the number of standards used are not an important factor to improve the error. Then we decided to use 3 standards freshly arrived from IAEA. One of them is the V-SMOW (Vienna Standard Mean Ocean Water) which define the 0 ‰ for the Oxygen 18 and the Deuterium and is the base to define the other standards in all studies in the world. We had the chance to use directly these standards which avoid the problems of a false determination of a sub-standard build by the laboratory. The other IAEA standards were **GISP** ($\delta_D = -24.76\text{‰}$ $\delta_{O18} = -189.5\text{‰}$) and **SLAP** ($\delta_D = -55.5\text{‰}$ $\delta_{O18} = -427.5\text{‰}$) (Figure 23).

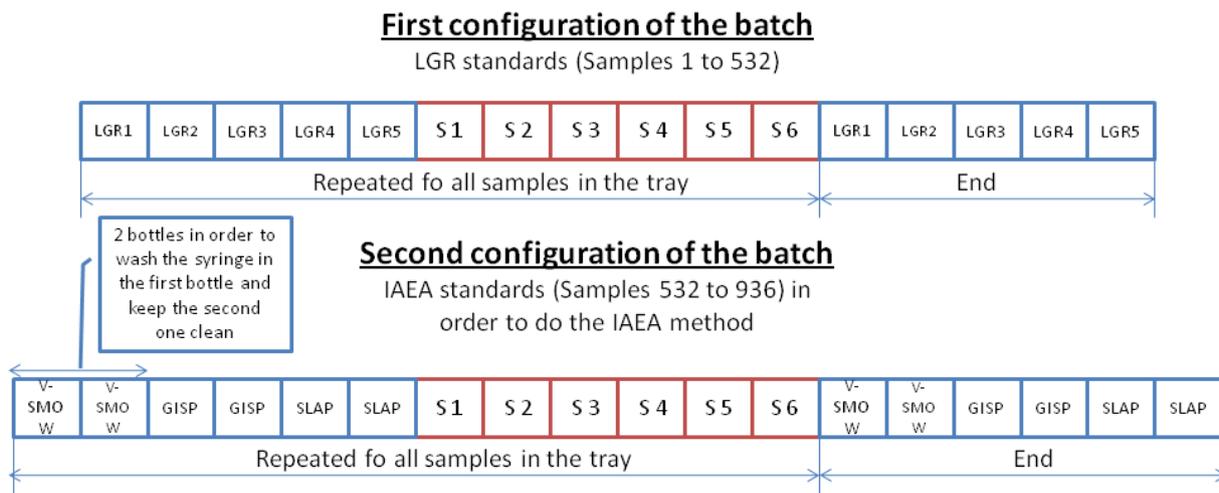


Figure 23 Schematic representation of vial arrangement in the tray

E. Post analysis

1. Attempts to reduce the error factors

In order to minimize and quantify the final error, a complete post analysis has to be done. We used matlab to analyze the data. Commonly the data are post analyzed by an excel table but it appears that to have more possibilities and to approach the minimum of error, matlab was more powerful.

All the methods we try are applied to the configuration that we used for our analysis ie. 6 samples between two standards - 6 injections per samples

a) The IAEA post analysis method

The *IAEA method* (IAEA 2009) consists in analyzing standards in order to quantify the gap before the analyzed samples (Figure 25). The value of this gap will be used for the next six samples until the next standards analysis. They will be used in the same way to determine the gap for the next samples and so on.

One or several blind samples are used to verify if this method is working. The blind samples are standards that we consider as unknown samples in order to approach, by calculation, the theoretical value.

In this method, the produced value from samples is determined by a simple average of the last 4 values of the injections.

This method was considered as a reference and all the methods that we try further were compared to this method.

Three remarks can be done on this post analysis method created per the IAEA. First, there is no consideration of the variation of the gap during one sequence of 6 samples. Then, it considers that the memory effect is inexistent after two injections. And finally, there is no quantification of the error but an approximation that is determined as $\pm 1\%$ for the δ_D and $\pm 0.2\%$ for the δ_{O18} .

- Precision calculation

To quantify the precision we used a normal batch within which were inserted blind samples.

The results gave a standard deviation of $\pm 0,2\%$ for one batch.

a) Hide the memory effect

We noticed that the evolution of the analysis looks like an exponential curve. We decided that it was interesting to fit an exponential function defined by " $f(x) = a * e^{\text{tau}*x} + b$ " to hide the memory effect. In that way, we used the Matlab function "lsqcurvefit" that allows to give the different parameters "a", "tau" et "b" thanks to an evolution. (Figure 24 Two following standards evolution and the the fitting with an exponential).

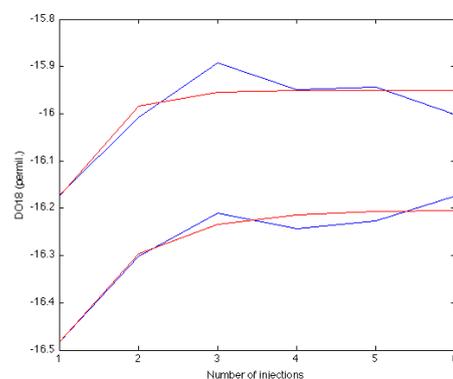


Figure 24 Two following standards evolution and the the fitting with an exponential

The “tau” is negative and represents the rapidity to reach the limit, the “b” represents the final value, “a+b” represents the initial value. “b”, the final value is the one that we consider as the value produced by the LWIA.

As the machine is doing the analysis in the same way, it was interesting to find a fitting with the same “tau”. If we prove that the “tau” is stable, then it will be possible to run the fitting with a fix “tau”. During one sequence, we fitted the exponential for 70 sample analysis with 12 injections. Unfortunately it happened that with this number of injection we didn’t find any stable “tau”.

Nevertheless, the last solution was to fit each evolution of the injections with the three parameters “a”, “b” et “tau”.

We did this method for one batch and we realized that the results given by the parameter “b” weren’t as stable as we wanted and didn’t give better results than a simple average of the last for samples.

b) Consideration of the gap variation between two standard analysis

The goal of this method is to consider the variation of the gap between two standards analysis. Indeed, the variation of the gap between standards analysis can be not insignificant (about 0.5 permil.). Thus, if you use the IAEA method, in some extreme case, you will give a value to the last sample of 0.5 permil., which is different from the real value. The idea was that the variation of the gap between the standards was linear and that we could give a virtual calculate gap for each sample (**Error! Reference source not found.**).

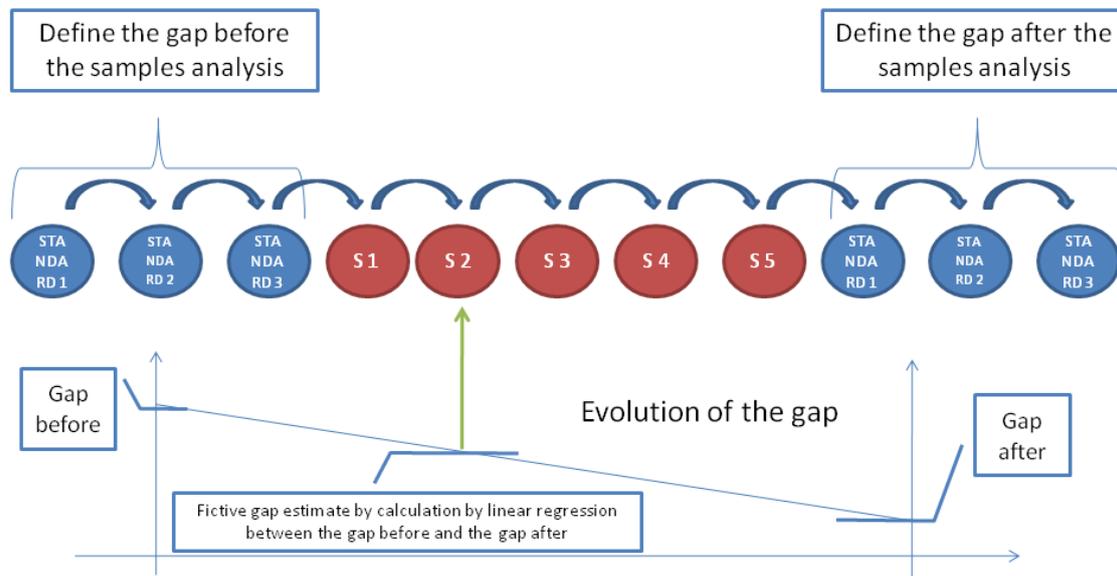


Figure 25 illustration of the process of the analysis of 5 samples and the gap (difference between the real value of the standards and the values given by the machine) variation effect

We succeeded to build a program with this method to analyze all the samples and the results were better than the IAEA method.

- Precision calculation

To quantify the error we used a normal batch within which were inserted blind samples.

The results gave a standard deviation of $\pm 0.13\text{‰}$ for the same batch that we used to determine the standard deviation for the IAEA method. This value means that this method of interpolation can really improve the results.

2. Precision

Previous investigations revealed different estimates for spectroscopy precision. The better precision is determined as $\pm 0.37\text{‰}$ for δ_D and $\pm 0.12\text{‰}$ for the δ_{O18} (Lyon 2009) (IAEA 2009) and the worse precision is determined as $\pm 1\text{‰}$ for the δ_D and $\pm 0.2\text{‰}$ for the δ_{O18} (IAEA, 2009). A recent paper (D. Penna 2010) compares different analysis to evaluate the LWIA method. It reveals that the analytical precision range from $\pm 0.56\text{‰}$ to 1.80‰ for δ_D and from $\pm 0.10\text{‰}$ to 0.27‰ for δ_{O18} .

In the previous analysis we just quantified the standard deviation for the δ_{O18} as ± 0.02 permil. This precision is not the one that we reached according to the comparison with the blind samples. It appeared that the precision could be very variable between each batch because of the variation of the gap. Then according to different test we realized, the worse standard is obtained for the first batches, which use the LGR standard. The deviation was roughly $\pm 0.2\text{‰}$ for the δ_{O18} . Considering the distribution as normal, the interval which contains 95% of the values is $\pm 0.4\text{‰}$. For the δ_D the standard deviation is about 1‰ and the interval which contains 95% of the values is roughly $\pm 2\text{‰}$. These values are not estimated by a strict probabilistic protocol but thanks to the comparison with blind samples analysis and their real value. We also compare the same batch analyzed several times.

For the last batches we used a better protocol with less uncertainty concerning the values of the standards and the reproducibility. Then we reach a standard deviation of $\pm 0.13\text{‰}$ (0.25‰ with the trust interval of 95%) for the δ_{O18} and 0.6‰ for the δ_D (1.2‰ with the trust interval of 95%).

F. Conclusion about the LWIA

To conclude with the LWIA, this new machine has the advantage to be faster than a mass spectrometer with a lower precision. Nevertheless this accuracy (0.27‰ for the δ_{O18} and 1.2‰ for the δ_D) is acceptable for a lot environmental study.

The main problem is the gap between the measured values and the theoretical values which can vary with different amplitudes. This gap is responsible for the precision and as this variability is not predictable the precision is variable for each sequence. Indeed, the precision of the instrument is much lower than the apparent accuracy (0.02‰ comparing to 0.27‰).

Advices for the followings measurements:

- Be careful of the pollution of the standards and so use one standard for one sequence of 5 samples or use the new method (Figure 25).
- No more than 6 samples between two standards analysis. No less than 6 injections.
- The best way to quantify the precision should be to evaluate it for each sample
- The method can be improved by a different way of analyzing:
 - Analyze more standards between samples for example one standard for one sample as (D. Penna 2010).
 - Use the regression to give a virtual gap as we did

VI. Results

A. Variables and accuracy of the variables

A part of the the numerical datas used for this thesis is annexed (*X ANNEXES Datas collected during the field trip with the SWI values of the samples*).

1. Direct measure

- a) **Length:** The lengths were measured by a simple regle which has a precision of $\pm 0.001\text{m}$. This regle was used to measure the length of the total cores. This regle was also used to cut the cores with the trowel. As this manipulation was delicate and adds different way of mistake the precision given is $2.5\text{cm} \pm 0.2\text{cm}$ and $5\text{cm} \pm 0.2\text{cm}$.
- b) **Global Position Satellite (GPS):** The instrument used to detect the GPS position is a GARMIN GPS, 12 Channel, Serial number : 36401900 (Garmin Olathe, KS, USA). The precision is given as $\pm 0.004^\circ$ for the latitude and the longitude which correspond roughly as a length of $\pm 200\text{m}$. This precision is admitted for the total core
- c) **Altitude:** The altitudes were found with the Google Earth application with a $\pm 15\text{m}$ vertical accuracy.
- d) **Weight:** Each sample were weight with a high precision balance with a precision of $\pm 0.001\text{ g}$. The bottom samples were often disturb and the weight of these samples has to be ignored.
- e) **$\delta_{O_{18}}$ and δ_D :** These datas are measure by the LWIA (Laser Water Isotopes Analyser) and the the precision of this instrument is widely discuss in the chapter *V. Material and method for the isotopic analyses* and more specifically in *V.E.2.Precision*. The accuracy is given considering an interval which conatins 95% of the values.
 - For the first configuration with the LGR standards (Figure 23): $\pm 0.4\text{ ‰}$ for the $\delta_{O_{18}}$ and $\pm 2\text{ ‰}$ for the δ_D
 - For the second configuration with the IAEA standards (Figure 23): $\pm 0.25\text{ ‰}$ for the $\delta_{O_{18}}$ and $\pm 1.2\text{ ‰}$ for the δ_D .

2. Measure from the Svartberget weather station at Vindeln Lat 64d 14' North, Long 19d 46' East

- a) **Temperature :** The air temperature is measured at 1.7 m above ground in open area. Method: Ventilated radiation shield. 60 sec scan, 10 min mean build daily temperature. For each day the maximum, the minimum and the average temperature are given. Precision : 0.01°C
- b) **Precipitation** (Snow and rain) : Manual routines, SMHI-standard gauge. The precision of this instrument is variable and about 0.3 % of the total amount of the snow can be missing because of the weather conditions.
- c) **Snowpack elevation :** Automatic recorder with ultrasonic sensor. Daily mean valued based on 60 min scan interval. Precision: $\pm 1\text{mm}$.
- d) **Wind :** The wind speed is measured 38 m



above ground, 16 m above old spruce forest.
10 sec scan, 10 min mean build daily values.
Max wind speed based on 10 sec scan.
Precision : +/-0.01m/s

Figure 26 Svarberget weather station

3. Calculated Variable

- a) **Volumes sampled** : The volumes of the samples are calculated as a semi cylinder (Figure 17 picture of the core with the scale in order to describe it to see the shape of the core) defined by the Russian corer radius with the formula :

$$\text{Volume} = \frac{\pi * (\text{Corer radius})^2}{2} * \text{Length}$$

Equation 2 Semi cylinder calculation

The radius of the Russian corer was measured as 0.024 m +/-0.001m. The volumes were calculate with a length of minimum 2.5cm +/-0.1cm (the samlest core resolution) . Then the precision of the volume is **+5 cm³**.

- b) **Density** : The density of each snow sample is determined with formula:

$$\text{Density} = \frac{\text{Weight of the snow sample}}{\text{Volume}}$$

Equation 3 Density calculation

For the 2.5cm resolution cores the precision of the density is evaluate as **+50kg/m³**. For the 5 cm resolution cores the precision of the density is evaluate as **+25kg/m³**. For the total core density the precision is evaluate as **+20kg/m³**.

- c) **Weighted mean** : $\delta_{O_{18}}$ and δ_D of the cut cores : in order to do a comparison between the total core and the cut cores for the isotopic value, a calculation is done to have the value of entire core. The formula is:

$$\delta_{SWI,tot} = \frac{\sum_{n=top}^{bottom} \delta_{SWI,n} * \text{Weight}_n}{\sum_{n=top}^{bottom} \text{Weight}_n}$$

Equation 4 Weighting $\delta_{O_{18}}$ and δ_D calculation

The accuracy of the same than the $\delta_{O_{18}}$ and δ_D considering that the accuracy on the weight is negligible (we can do this approximation because the balance was a high precision balance):

- If "a" is the value to weight with an accuracy of $\pm e_a$ and "p" the weight

$$a_{tot,max} = \frac{\sum_n (a_n + e_a) * (p_n)}{\sum_n (p_n)} = \frac{\sum_n (a_n * p_n)}{\sum_n (p_n)} + \frac{e_a * \sum_n (p_n)}{\sum_n (p_n)} = a_{tot} + e_a$$

Equation 5 Demonstration of the accuracy value for the weighted mean

Then the accuracy of this value is roughly **+0.4 ‰ for the $\delta_{O_{18}}$** and **+2 ‰ for the δ_D** .

B. $\delta_{O_{18}}$ and δ_D data - statistical analysis

936 samples were analyze for the $\delta_{O_{18}}$ and the δ_D . Basic statistical results are presented in order to have an overall idea of this dataset. For the $\delta_{O_{18}}$ the average values is **-18.18** and the standard deviation is **3.22**. For the δ_D the average values is **-130.95** and the standard deviation is **26.50**. The two histograms for the δ_D and the $\delta_{O_{18}}$ show the same appearance because the same processes acts on the Oxygen 18 and the Deuterium during the condensation and the distillation. Values range between **-25‰ and -10‰** for $\delta_{O_{18}}$ and -

200‰ and -50‰ for δ_D . This range is the typical range for cooler region characterized by more depleted values and therefore the melted snow values at this latitude.

The δ_D and δ_{O18} composition of the snow samples (Figure 27) from the dataset show that the isotopic composition for almost all waters lie or close the Global Meteoric Water Line (GMWL, (Craig, 1961)). Since the snow appears to be not affected by the evaporation and moreover the temperatures exceed rarely 0°C, The Local Meteoric Water Line for the region was determined from a linear regression of the dataset. The equation of the LMWL is $\delta_D = 8,1177 * \delta_{O18} + 16,63$, which a slope close to the GMWL. Overall, data plot close to the GMWL, suggesting that the samples are insignificantly affected by isotopic enrichment due to evaporation.

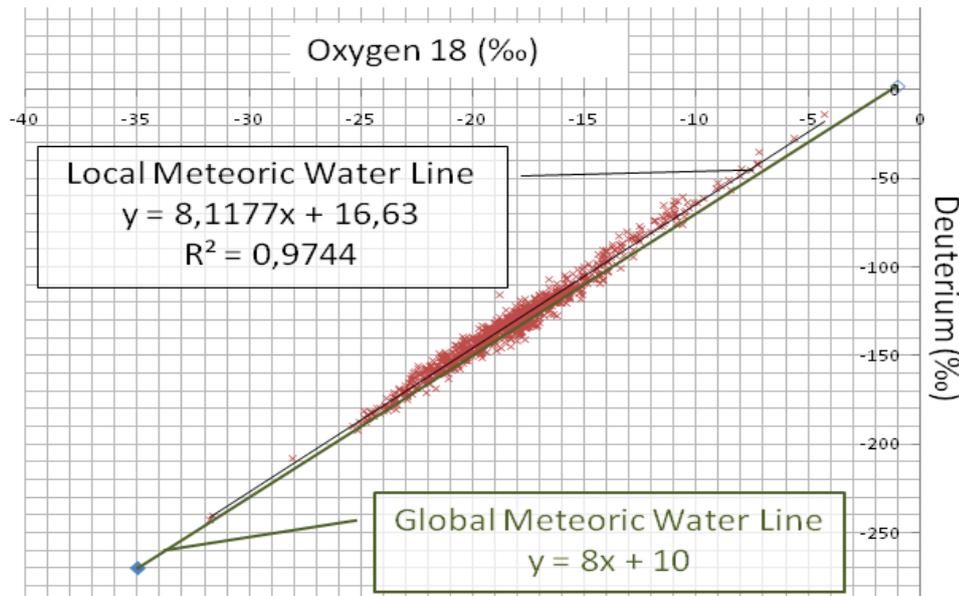


Figure 27 Plot of the δ_D versus δ_{O18} values from snow packs over Sweden during the field trip (2009/2010), shown in relation to the Global Meteoric Water Line (Craig, Isotopic variations in meteoric waters, 1961). The Local Meteoric Water Line is determined from a linear regression of all the snow pack values in the studied area.

A. Total core results interpretation

1. spatial interpolation method

Snow depth and total core value of δ_{O18} and δ_D were measured for the 64 cores spread over about 300 000 square km. (Figure 14 View of the different sites studied in the past (Bergman, 1980, Allan Rodhe, 1987). Position of the weather stations which measure the snow depth. Areas of sampling planned before the field trip with the name of the different places in blue. Position of samplings realized (the red crosses). The background of this map represent the average of the Oxygen 18 between 1975 and 1980 thanks to a kriging build from the Burgman data. Two method of interpolation were used to draw the map (thanks to the software ArcGis®): The Inverse Distance Weight and the Kriging.

- The Inverse Distance Weight is base on a mathematic formula. each point on the map is a linear combination of the known point. The more the distance is high between a point $M(x,y)$ and a knan point the more the weight will be low. Thus the relation is build on the formula :

$$Z(x) = \sum_{i=1}^{\text{number of point}} \frac{\text{weight}(i)(x)}{\sum_{j=1}^{\text{number of point}} \text{weight}(j)}$$

The weight is defined by $\text{weight}(i)(x) = \frac{1}{(x_i - x)^n}$, the power “n” is determinate empirically.

Equation 6 Inverse Distance Weighting formula

- The Krigging is a less determinist method. Indeed the idea is to estimate statistical parameters from data and not impose a mathematic formula which could be inadequate. This method is powerful because you use the best interpolation that you could have and you can have an idea of the interpolation accuracy. We will not present the methodology here because it’s too complex but you can refer to (Journel 1989) or (Arcgis : How kriging works 2008) for more information about the krigging and the way how ArcGis build the interpolation. For our interpolation we chose, thanks to the ArcGis help, the following parameter : **Kriging method : ordinary; Semi variogram model: spherical; Points build from the 12 first neighbors.**

2. Snow depth

We draw the map representing the snow depth in order to compare the results of the field trip and the map draw by the SMHI (Figure 28 and Figure 29). We confirm the fact that the snow depth was anormaly high for this region. Furthermore, there is a good correlation between the two maps. This correlation confirms that the few area (24) where we collected information can be enough to predict the spatial variation over the 300 000 square kilometers.

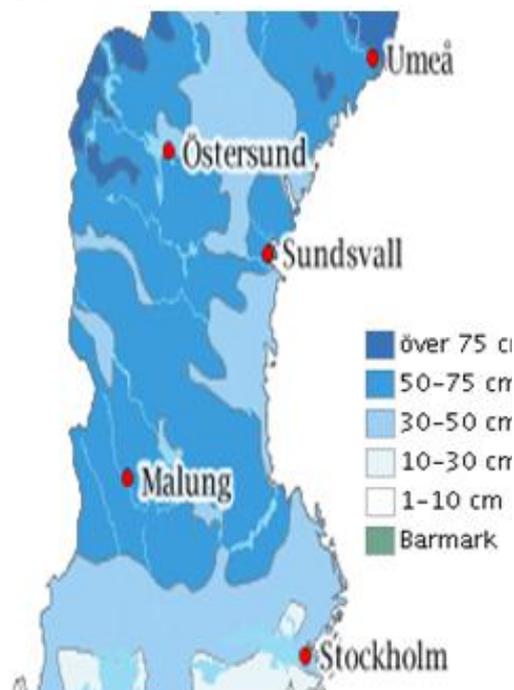


Figure 28 Snowdepth mesured and interpolate by the SMHI for 23th march (closest date of the end of the field trip)

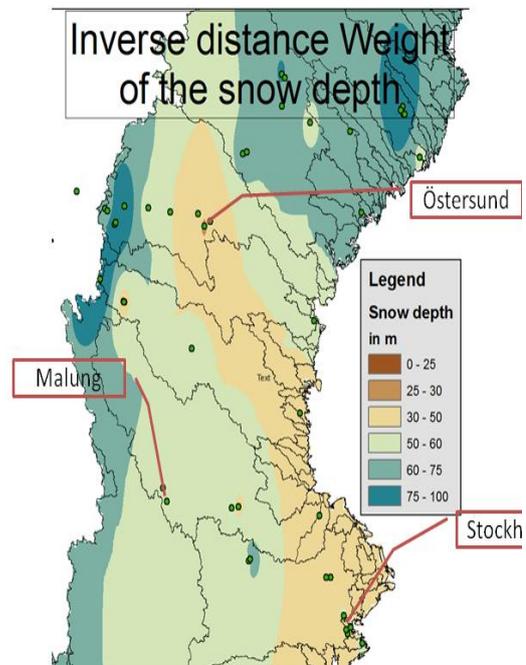


Figure 29 Snow depth measured during the field trip and interpolated thanks to the Inverse Distance Weight method with ArcGis

3. Oxygen 18 and Deuterium Spatial variation

To assess these maps we suppose that no cores were significantly disturbed during the winter season and the total core SWI signal reflects the average signal in the snowfalls during winter for the DJFM (December January February March) season. This hypothesis is admissible because the temperature exceeded rarely 0°C between the first snowfalls in December and the sampling period in March in the most southerly place : in Stockholm, (Figure 8).

The both, $\delta_{O_{18}}$ and δ_D spatial variation were plotted (**Error! Reference source not found.**). These two maps give the same evolution because the same processes act on the Oxygen 18 and the Deuterium during the condensation and the distillation. Thereby, the consistency of the results is demonstrated by these two maps. Further, considering this assessment, we will not discuss about the Deuterium variations but only the Oxygen 18 variation.

Oxygen 18 ranges from $\delta_{O_{18}} = -12\text{‰}$ in the Trondheim region to -19‰ in the Stockholm region and in the north. According to the Burgman sampling campaign between 1975 and 1980 the $\delta_{O_{18}}$ during DJF and for the entire year, shows the latitudinal gradient was prominent versus the longitudinal gradient (Figure 12 and Figure 30). However, in the current study, the values of the latitudinal gradient are non-evident while the longitudinal gradient is largely visible. These results confirm the outputs of the REMO-ISO model (Figure 7) which shows, for 40 years of simulation, that the Oxygen 18 pattern in the precipitation is principally governed by the westerly air masses effect.

These results show for the first time the westerly air masses effect from the Atlantic according to only analyzed samples.

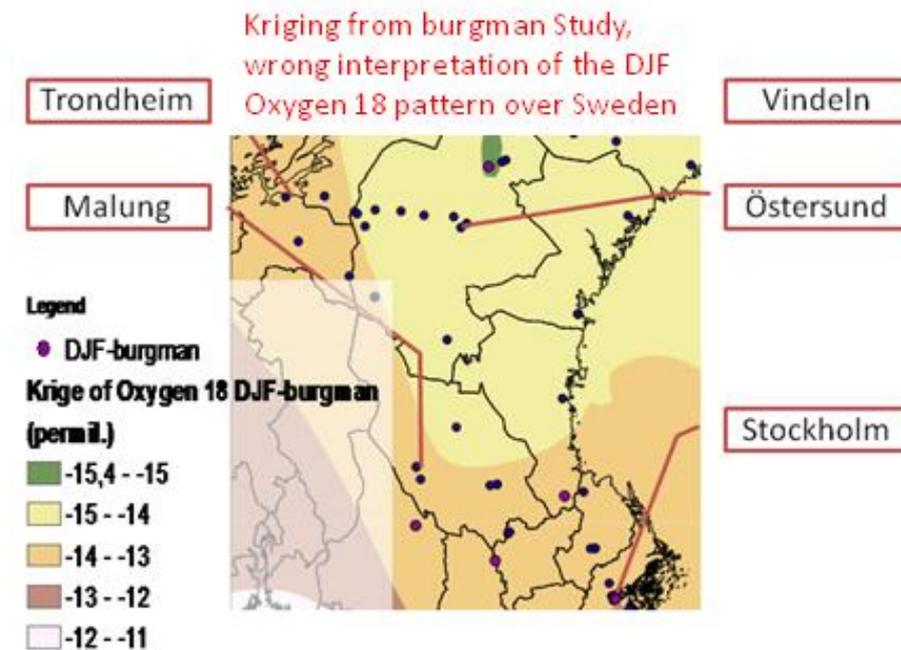


Figure 30 Spatial variation of the Oxygen 18 only for the December January February from (Burgman, et al. Dec 1981) with a data set of 5 years (1975 1980). Bad interpretation because there were not enough data.

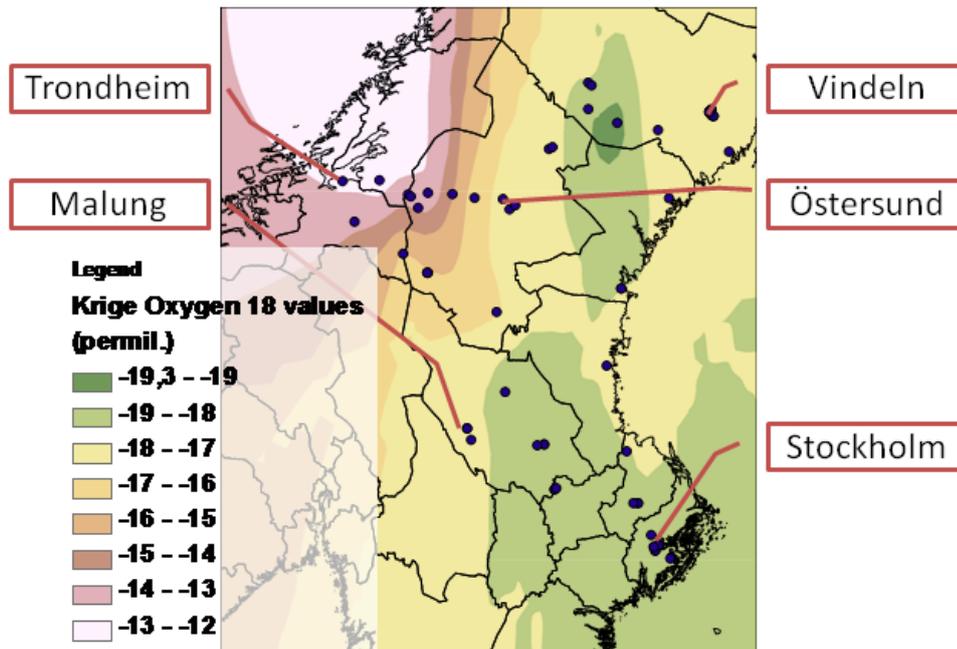


Figure 31 Krige of Oxygen 18 values from 64 total core sampled during the field trip (16/03/2010 to 26/03/2010)

4. Longitudinal variation around the 63.5°N latitude

The window 63.5°N±1° latitude (Figure 4) was chosen because of the high concentration of measure in this area. The evolution of the total core δ_{O18} (with the δ_{O18} recomposed total core build with a weighting of the stratigraphied cores and the outputs of the REMOiso model), the elevation and the latitude with the longitude are plotted in order to describe the processes.

The longitudinal δ_{O18} values (at latitude 63°N, Trondheim–Östersund-Umea line, Figure 32) reach from $\delta_{O18}=-10$ ‰ in Trondheim region to -19 ‰ in the center of Sweden. The values globally decrease from the east to the west. This evolution shows the westerly air mass effect. Indeed the air masses, charged in humidity from the Atlantic ocean come across the fjord in Norway and discharge a huge quantity of precipitation on the Scandinavia mountains by the Foehn effect. When the air mass goes past the mountain this is the Rayleigh distillation process which govern the δ_{O18} evolution. δ_{O18} evolution decrease until the longitude 17°W (close to Östersund) with roughly -19 ‰. For the higher longitude the evolution seems to increase to -17 ‰. This increase is probably due to the proximity with the Baltic See which bring mostly see water with a higher δ_{O18} composition.

This evolution is confirmed by both the recomposed cores with weighting method from the stratigraphied cores and the REMO-ISO outputs from 40 years of simulation.

5. A mark of the very negativ NAO index in the snow pack

For the most NAO negative years (NAO-) and the most NAO positive years (NAO+) between 1959 and 1999 (see selected years on the Figure 7), the δ_{O18} is plotted around the average. This work was done in order to see the effect of the NAO on the SWI signal in the snowpack.

Between 10°E and 14°E the deviation between the NAO- and the NAO+ is insignificant and can explain why the difference between the average and the 09/10 winter values is low. Nevertheless, the influence of the NAO seems to be more significant from 14°E to 20°E.

Indeed, the analyzed cores $\delta_{O^{18}}$ evolution in this longitude range for 09/10 winter (which is the lowest NAO index record for 180 years of recording) is much lower than the tendency (about 2‰). This position seems to be normal because the $\delta_{O^{18}}$ for the NAO- tendency is also lower. The very low and unusual values for the 09/10 winter can be explained physically by a bigger contribution of air masses from the north with a lower $\delta_{O^{18}}$ values. This flux from the north is often explained with a NAO negative index, this flux brings colder and drier weather than usual. But, counter to this theory this year wasn't drier than usual with for example in Umea for DJF a total amount of 170 mm of precipitation which is more than the average (140mm). Thus, this example shows the limit of the NAO to explain the regional variability of the precipitation.

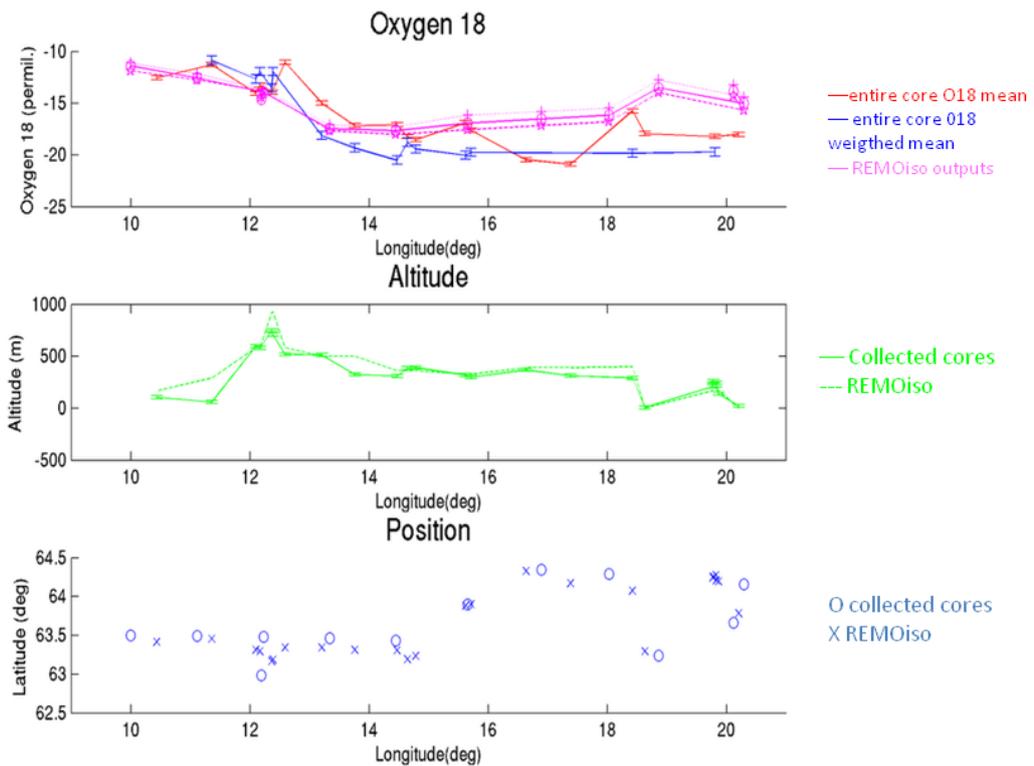


Figure 32 Variability of the $\delta_{O^{18}}$ with the longitude in the snow pack and comparison with the REMOiso outputs. 1) Bottom: position of the sampled cores (cross) and position of the REMOiso outputs (circle) define as the nearest neighbors of the sampled cores. 2) Middle; Altitude for the position of both the sampled core (solid green line) and REMOiso position (dashed line). 3) Top: red line represent the Oxygen 18 variation in the entire core, the blue line represent the Oxygen 18 variation in the entire core recomposed by the weighted mean of the cut cores. The pink line represent the REMOiso DJF outputs for 40 years of simulation. The "+" line represents the evolution for the most NAO positive years. The "-" line represents the evolution for the most NAO negative years (see the chronology in Figure 7).

B. Post-depositional modification of stable isotopes in svart berget

1. Validation the raw vertical δ_{O18} signal

To validate our results we realize, for the same site, two 5cm resolution replicates for one 2.5cm resolution cores. We choose 3 sites, Uppsala (lat=59.8° long: 17.5°, Figure 33), Borlänge (lat=60.52° long: 15.53°, Figure 34) and Vindeln (lat: 64.2° long 19.8°, Figure 35) (to represent the vertical δ_{O18} signal (and)). The correlation between the three replicates is good, indeed the same evolution is observed for the 3 replicates. For the Uppsala site, the two first cores of each site were realized in the same field, that's why the correlation is better for the two first cores. The third one (green line) was collected outside of the city and the snowpack elevation is therefore higher and the signal is shifted.

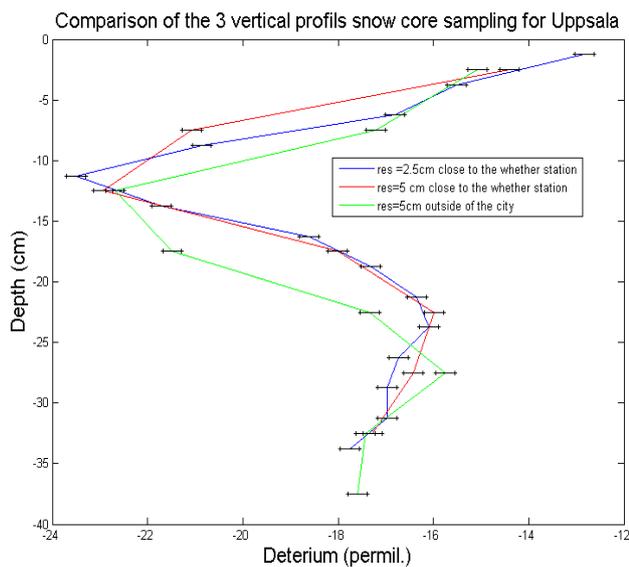


Figure 33 δ_{O18} signal with the depth in Uppsala (lat=59.8° long: 17.5°) the 16th March. 2 cores with different resolution (red and blue lines) are collected in the same area. The last one (green) is collected in a field outside the city. The accuracy is represented in black.

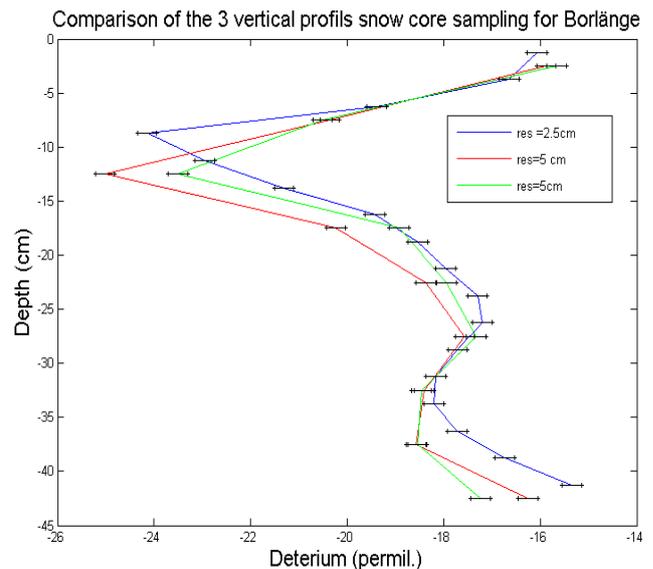


Figure 34 δ_{O18} signal with the depth in Borlänge (lat=60.52° long: 15.53°) the 17th March. 2 cores with different resolution (red and blue lines) are collected in the same area. The last one (green) is collected 5 km further. The accuracy of the δ_{O18} measurement is represented in black.

There is a good concordance between δ_{O18} profiles between the Uppsala and Borlänge away from 100km). This finding suggests that the δ_{O18} stratigraphy of the snowpacks is the result of large scale snow event.

2. Validation the raw vertical density signal

The density signal has been plotted for the Vindeln site (lat: 64.2° long 19.8°, Figure 35). According to the accuracy of +25 kg/m³, the 3 cores present different evolution but vary in the same range according to the low accuracy. Two different parts can be identified, the upper layer (0-10 cm) which correspond to the fresh snow with a density range from 100 to 200 kg/m³ and the depth layer (10-75cm) with a density range from 200 to 350 kg/m³. No clear relationship exists between the snow layers given by the comments (except the fresh snow) and the density.

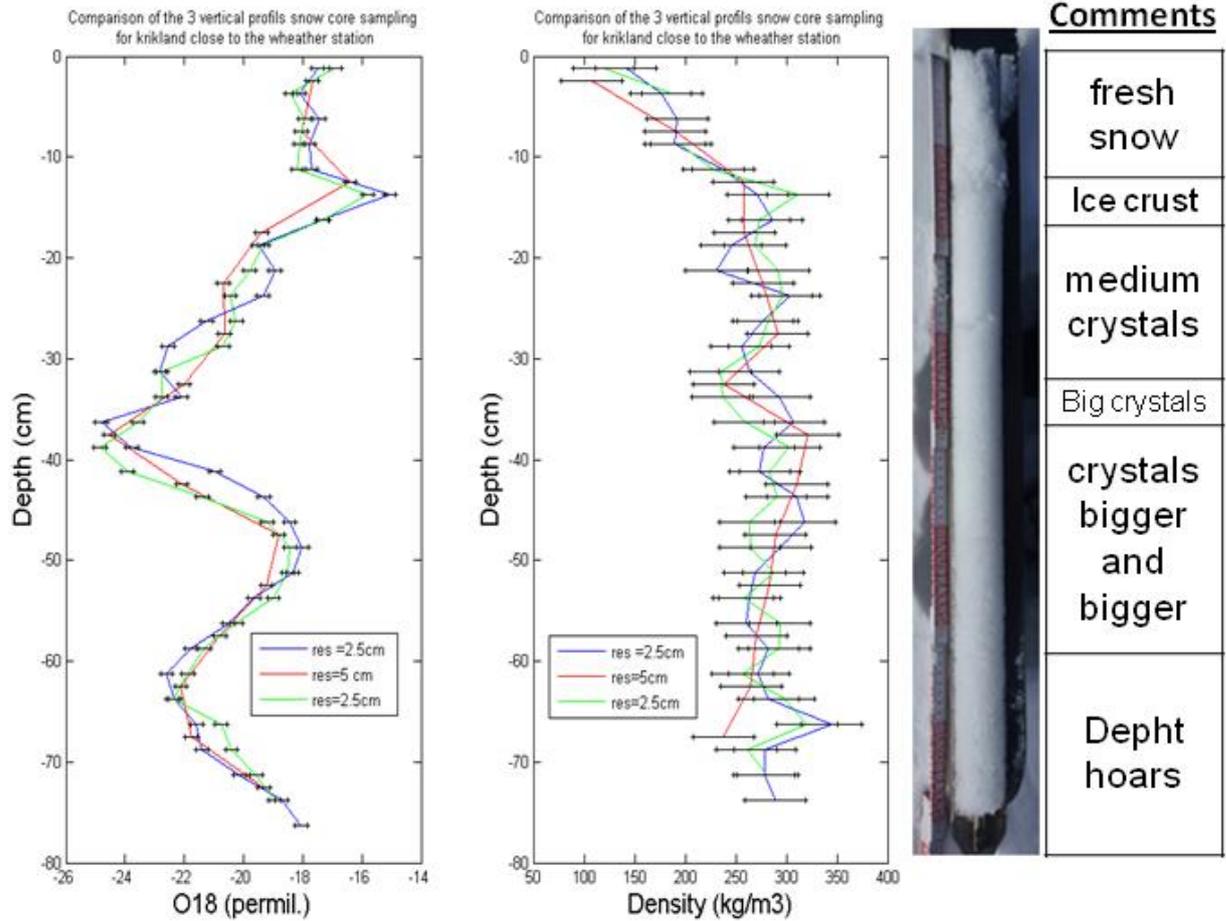


Figure 35 δ_{O18} (left) and density (middle) variability with the depth in Vindeln (Svartberget field station) (lat=64.2° long: 19.8°) the 24th March. 3 cores, 2 with a 2.5 cm resolution and 1 with 5cm resolution were collected in the same open field area close to the weather station. To the left, the picture of the first 2.5 resolution core (blue line) has been dressed with the same scale as the graphs with the comments written during the field trip.

C. Datation of the cores in Svartberget Station (Vindeln)

1. Weather conditions during the snowpack formation

These part attempts to assess to which extent the snow cores/profiles provide a record of the winter precipitation. This assess need a good understanding of the different weather impact which can modify the snow pack. In the Svartberget Field Station the followings parameters are measured: the temperature, the wind speed, the precipitation, the type of precipitation and finally the recording of the snowpack depth (Figure 36). No rain event were recorded during this winter, moreover the temperature exceed rarely 0°C. Therefore, the snow pack is more influenced by the compaction than the melting. Nevertheless, the temperature seems to have an impact for the 03/03/2010- 10/03/2010 because the maximums exceed 0°C and the snowpack drop dramatically in comparison with the last compactations, this idea is confirmed by the ice crust seen on the core (Figure 35). On the other hand, the very low temperature during the 25/01/2010- 5/02/2010 period could be responsible of a very low compaction (observable on the snow depth). Regarding the wind variability, there is no direct obvious impact of this parameter on the snow depth evolution.

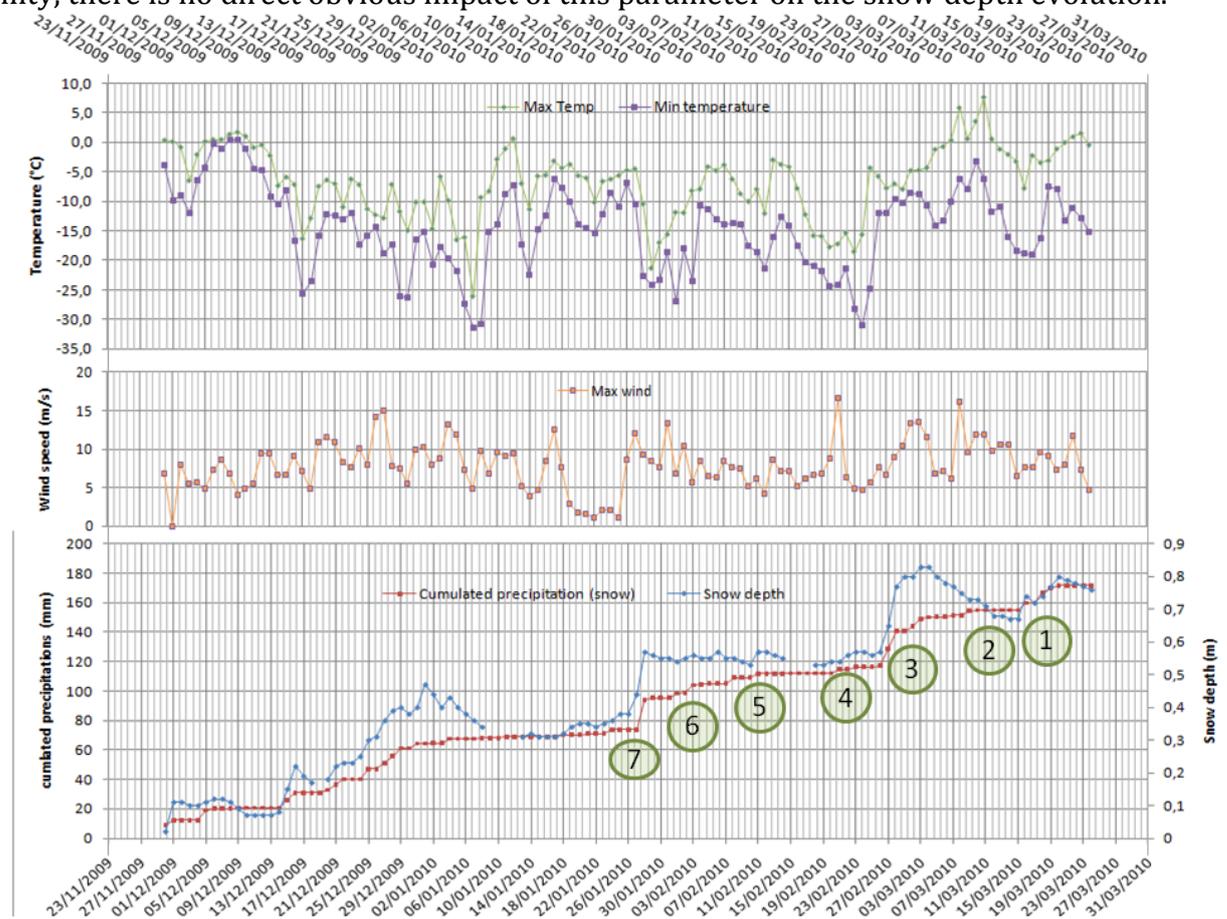


Figure 36 Climate information since the formation of the snow pack the 23th October 2009 to the date of the snow sampling in Svarberget Station the 24th of March 2010. 1) top : The maximum and minimum variation. 2) middle : the maximum wind variation. 3) bottom : The cumulated precipitation (red) and the snow depth (blue) evolution. The numbers correspond to the datation work and are used in the part 3. Datation.

2. Comparison of the $\delta_{O^{18}}$ in the stratigraphied core and in the collected snowfalls

Figure 37 shows the $\delta_{O^{18}}$ profile from the Svart Berget weather station field in the 2009/2010 accumulation season from the 23th October to the 23th March. Both the snow core collected and deposited partially sampled are represented. The depth is represented as a snow water equivalent (SWE) tanks to the density values and is measured from the surface to the base of the snow pit. No error bar were plotted but the Figure 35 can give an idea of both the error on the $\delta_{O^{18}}$ and on the density. As we did not sample continuously, we cannot be sure that we measured the true isotopic peaks (either negative or positive). This resolution is sufficient to track the isotopic character of major snowfall events through the accumulation season, but small snow accumulation will be missed or averaged with larger events.

There was a wide range in $\delta_{O^{18}}$ values of the snow core, with the maximum seasonal range in $\delta_{O^{18}}$ averaging -24.8‰ and the minimum averaging -15.1‰ . For the deposited snow the values of $\delta_{O^{18}}$ range from -13.4‰ to -29.4‰ . The values of the precipitations have a bigger frame than the core values because the core values are smoothed because of the mix of the upper layer with the wind, the compaction and because of the melting.

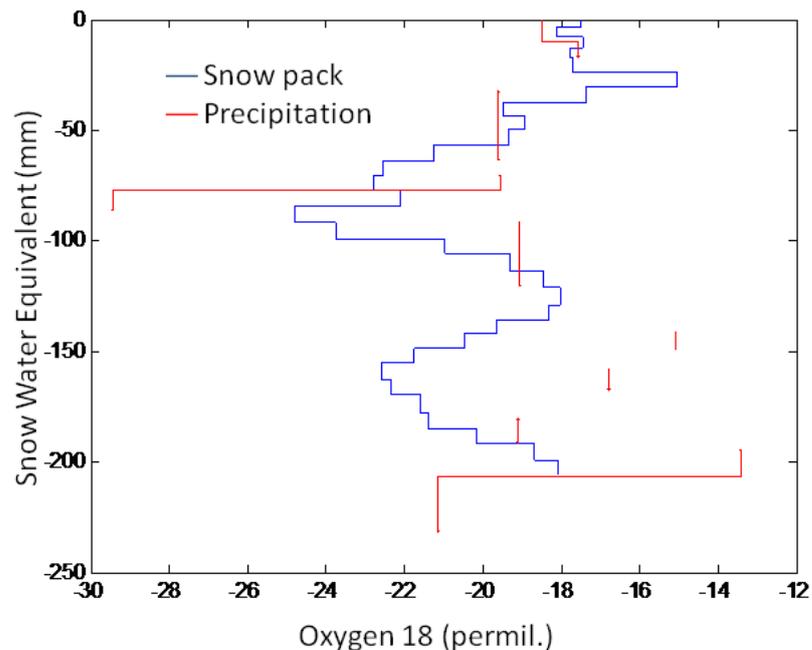


Figure 37 $\delta_{O^{18}}$ values of the different layer in the cores and $\delta_{O^{18}}$ values of deposited snow as a function of Water Equivalent. The deposited snow is partially recorded because of the low accumulation of some snow event and technical problems. No error bars are plotted here but you can refer to Figure 35 to have an idea of the error.

For the last 120mm of deposited snow (corresponding to the first 50cm depth from the top) the range of $\delta_{O^{18}}$ is similar for the deposited snow analysis and for the snow core. The maximum of 29.4‰ for a little snow event has been smoothed by the less depleted snow events framing this event, we observe similar difference in the (Figure 2) from (RODHE 1987).

Deeper, the relation is less obvious. The difference of the total amount can be explain by melting or by a wrong determination of the snow amount by the instrument (it is known that one can lose up to 20% of the total amount of snowfall with a rain gauge). In all case, no snow event sampled can explain the maximum of -22.9‰ at the SWE of 155mm. It is

probably an uncollected snow event which made this maximum or a sampling error. Indeed, if we compare this evolution with the (Figure 2), where the conditions were similar, nothing can explain this difference in the depth.

3. Datation

For the datation, only the first 50cm depth from the top were considered according to the last conclusions. The maximum between 12.5cm and 15cm correspond to the iced crust which appears on the core and were notice in the comments (Figure 35). As there is hole in the collected snow event we can't argue that there is an enrichment in this sample because of the melting (during the fusion of the ice the Oxygen 18 stay longer in a iced state) . Moreover when we see the evolution of the temperature and the snow events we observe that this maximum corresponds to a snow event with higher temperature. Plot the temperature with the SWE equivalent can give an idea of the temperature during the different snow events (Figure 38). As the temperature is the principal parameter responsible of the SWI composition, the temperature evolution is a good indicator to detect the different event in the SWI signal from the snow core. Indeed, we detect 7 snow events, easily and properly thanks to this method.

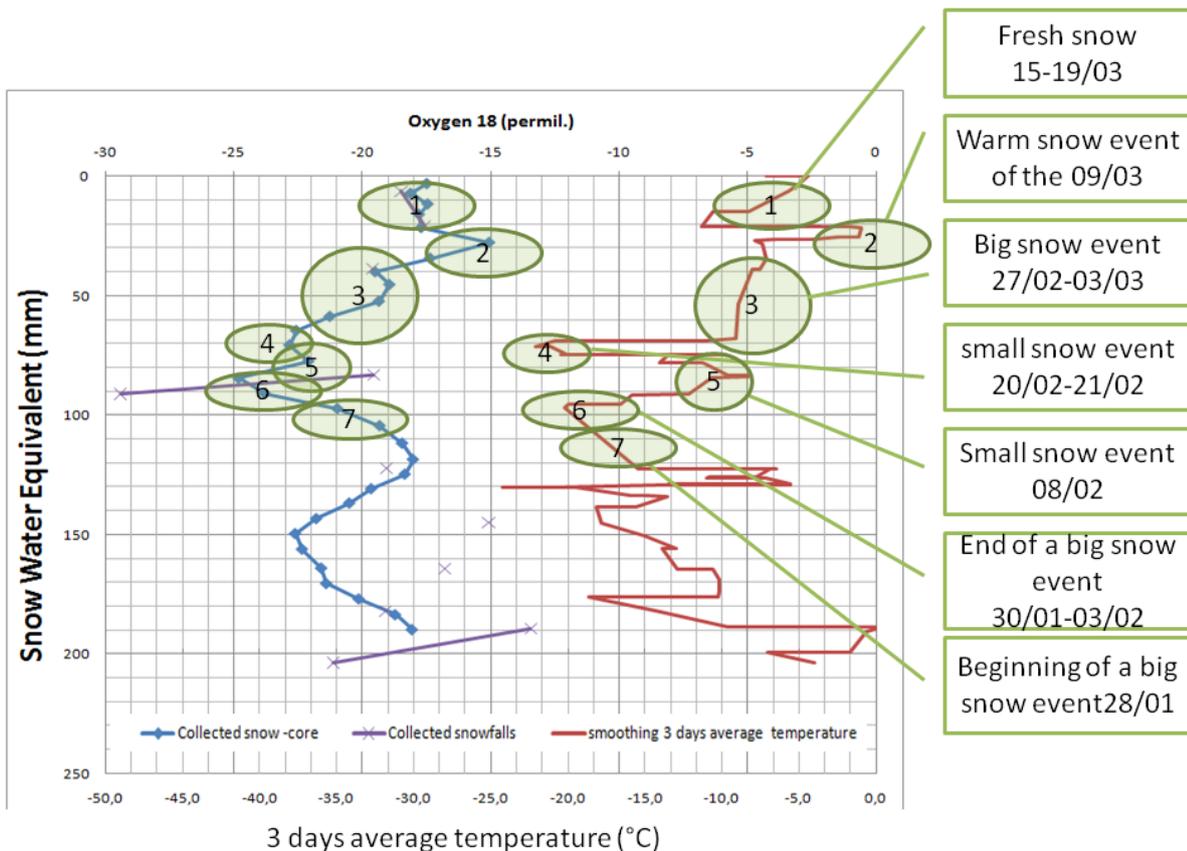


Figure 38 Datation of the core with the 3 days average temperature as function of the Snow Water Equivalent evolution. Each correspondance snow event-composition in δ_{O18} can be identify from this graph with a confirmation of the snow pack evolution. In total 7 events were indentified, The deep of the snowpack was too smoothed and doest not compare properly the two signal.

Give for each snow piece an exact datation is difficult. Nevertheless we can easily give an approximate value for each event. For example we can assess that the 4 first cut of the core (10 first cm) are from the snow events between the 15 and the 19/03 and correspond to a $\delta_{O_{18}}$ value ranging between -17‰ and -18‰. Between two distinguishable event the values of the core piece is non identifiable because it's probably a mix of two different snow. Finally, we can process to a datation with a variable precision depending of :

- The depth of the piece of core (fresh snow is easily identifiable the deeper levels)
- The duration of the event (one event on several days will give a different SWI signal than a big and fast event)
- The difference in terms of SWI signal between the events (if the signal is in the same range, no events will be identifiable)
- The size of the snow event (the size must be 2 times bigger than the core resolution (more than 4 mm) to be identifiable, if not the event can be divided in two different piece of core and be smoothed with other events)

VII. Conclusion

Based on the results from $\delta_{O^{18}}$ and δ_D analyses of the snow cores collected in Sweden (and in Norway) over a triangle whose vertices are Umeå, Trondheim and Stockholm, this study concludes that this new methodology to measure the isotopic signal coupled with the new technology has a very big potential. Moreover, this exceptional winter is characterized by a very high snow depth in the studied area and globally the lowest negative NAO (North Atlantic Oscillation) index for the winter season never measured before. These two facts provided an extraordinary opportunity to record and document this winter.

An important part of this study was devoted to the practical side to facilitate future similar work by a complete explanation of the different protocols. Indeed, a new methodology to sample a maximum of snowpacks in a minimum of time was presented in order to use the new possibilities of the Laser Water Isotopes Analyser (LWIA). Moreover, the capacity of the LWIA and its limits were discussed, to define the accuracy and treat properly the raw data.

Overall, the results reveal the East-West SWI gradient of the SWI signal in the accumulated snowfalls during the winter. This gradient is explained by the westerly airmasses (Atlantic) modeled by the REMOiso model but never measured. These results update our understanding of the SWI signal repartition in this region which was mostly explained by the latitudinal effect (Burgman, et al. Dec 1981). $\delta_{O^{18}}$ outputs from the REMOiso model on the same latitude (63.5°N) were analyzed in order to compare the low and high NAO index years' influence on the snowpack SWI signal. It emerged from this comparison that the current year is clearly defined by a very low NAO index regarding only the measured signal. Moreover, the isotopic values at this latitude are 2‰ more depleted than the $\delta_{O^{18}}$ values extract from the most NAO negative years and extract from the Burgman study. This findings confirm the very exceptional climate circulation during the winter of 2009/2010 .

Furthermore, the common structure of the vertical $\delta_{O^{18}}$ profiles selected in 3 different sites show the repeatability of the measure and the homogeneity of the snow packs between very close cores (less than 5km). The concordance between $\delta_{O^{18}}$ profiles at sites 100km apart in Uppsala-Brolänge region suggests that the $\delta_{O^{18}}$ stratigraphy of the snow packs is the result of regional synoptic controls. The datation attempts made in Svartberget weather station thanks to a complete measuring of the climate condition during the snowpack formation and an isotopes record of the snowfalls, highlight the role of the temperature as an indicator of the different SWI composition in the cores.

Finally, this work shows the feasibility of carrying out a 6-month field campaign with analysis and interpretation of 936 samples.

VIII. Outlooks

For this work, analysis of the huge dataset (23 sites 64 stratigraphied cores and 936 samples) has not been completely achieved. Indeed, different work was necessary and took time to achieve (methodology of the sampling, start-up of the LWIA, writing the algorithms to treat the data). This work done, future work on similar lines could be effected more easily. Nevertheless, the quantity of data was high for this study ; to keep the same quantity of samples to analyze them in one year is sufficient. At a later time, sampling for the longitudinal effect around the 63.5°N parallel could give an idea of the evolution of this value and compare it with REMOiso outputs in order to detect the NAO signal.

Furthermore, the REMOiso model could be used in order to compare the results from the modelisation and the direct measure. Such an endeavour needs global climate dataset that we cannot obtain before a few years have elapsed.

Finally, an important task will be to establish an age-depth model for the snow cores, so that we can reconstruct the history of snow events. In theory, if we know the time and amount of precipitation (alt. evolution of the snowpack depth) throughout the season, it will be possible to reconstruct the evolution of the snowpack, and thereby attribute a date to the 2.5 cm slices with known d18O and density. Moreover, we have established that plotting the temperature as a function of the snow accumulation is a good way to differentiate the snow events. The observational information from SMHI covers all of Sweden, and this model could be tested on Kryklan where we independently know the δ_{O18} in the precipitation.

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B. Sverberget Field Station (Vindeln) Data (only a part)

1. Stable Water Isotope signal in the precipitation (only a part)

The snow events (and some rain event) were partially sampled in order to analyze the SWI composition. 67 % of the snow events were sampled. Some snow events were not sampled because of the low amount of snow or eventual technical problems of single events that we try to reconstruct).

date	konduktivitet	temp grader	pH	temp grader	sno regn	comments	δD (‰)	δD ‰	Quantity	cumulated
07/09/2005	3,69	12,2	4,91	11,4	R	5,6mm			5,6	5,6
09/09/2005	4,13	17,6	4,95	12,5	R	4,5mm			4,5	10,1
20/09/2005	4,62	17,7	5,36	13,2	R	3 dagas 3,6mm			3,6	13,7
22/09/2005	4,12	18,3	4,98	16,6	R	4,3mm			4,3	18
24/09/2005	R	0,2mm			0,2	18,2
27/09/2005	6,41	18,4	5,26	17,3	R	0,5mm			0,5	18,7
29/09/2005	4,07	21,4	5,44	18,3	Sno	2 dag 2,4mm	-10,85815	-70,780215	2,4	21,1
04/10/2005	2,72	20,1	5,3	17,1	R/S	3 dag 11,5mm	-18,1368	-133,12555	11,5	32,6
06/10/2005	24,2	15,6	5,29	10,2	R/S	18mm	-17,82235	-132,6352	18	50,6
15/10/2005	2,28	13,8	5,23	13,2	R	13,1mm	-15,7854	-119,5837	13,1	63,7
19/10/2005	7,18	20,2	5,09	18	S	2,4mm			2,4	66,1
21/10/2005	14,84	18,8	4,35	15,8	R	0,5mm			0,5	66,6
22/10/2005	10,87	21,8	4,43	20,1	S	0,6mm			0,6	67,2
25/10/2005	12,99	21,3	4,33	19,4	R	3 dag 4,8mm	-11,6497	-78,068595	4,8	72
03/11/2005	13,49	19,4	4,55	17,3	R	1,3mm			1,3	73,3
08/11/2005	21,4	20,6	4,8	14,9	S	3 dag 6,3mm	-22,72845	-168,9888	6,3	79,6
10/11/2005	12,47	20,4	4,84	20,4	S	0,7mm			0,7	80,3
15/11/2005	7,43	20	4,64	20,1	S/R	3 dag 10,0mm	-14,41205	-102,83675	10	90,3
16/11/2005	6,6	14,2	4,55	13,2	R	5,7mm	-15,6567	-113,1111	5,7	96
17/11/2005	8,04	17	4,61	15,2	R	3,2mm			3,2	99,2
19/11/2005	5,6	16,3	4,7	14,8	R	4,5mm	-17,667	-133,44935	4,5	103,7
22/11/2005	4,36	20,8	5,08	20,7	R	3 dag 21,9mm	-16,50025	-123,8537	21,9	125,6
23/11/2005	R	1,8mm			1,8	127,4
24/11/2005	6,64	17,6	4,65	16,4	R	3,7mm			3,7	131,1
25/11/2005	4,47	13,7	4,87	14	R	13,1mm	-15,68805	-116,3937	13,1	144,2
29/11/2005	R+S	3 dag 1,7mm			1,7	145,9
30/11/2005	2,56	14,4	5,36	12,9	S+R	17,1mm	-21,13365	-158,8124		
06/12/2005	9,83	19,5	4,51	19,4	S+R	3 dag 7,6mm	-13,4401			
14/12/2005	S	2,8mm				
15/12/2005	3,28	21	5,05	21	S	6,7mm				
20/12/2005	6,45	18,6	4,97	19	S	3 dag				
21/12/2005	4,55	19,7	5,07	19,9	S					

Résumé

Des échantillons de neige saisonnière ont été collectés en Scandinavie entre les latitudes 59°N et 65°N. L'hiver 2009/2010 a été marqué, dans la zone d'étude, par une exceptionnelle hauteur de neige et par un indice NAO (North Atlantic Oscillation) le plus bas jamais enregistré (180 années d'enregistrement). La région reçoit des précipitations principalement d'origine atlantique, à l'ouest mais aussi d'origine baltique, au nord est. J'ai collecté 936 échantillons prélevés sur 24 sites sur une surface d'environ 300000 kilomètres carrés du 4 mars au 26 mars 2010 en voiture. Au total 128 carottes ont été récupérées, et la moitié d'entre elles découpé, pour mesurer la densité et pour une analyse en isotopes stables de l'eau (Oxygène 18 ($\delta_{O^{18}}$) et Deutérium (δ_D) connu sous le terme de SWI) pour chaque couche. L'énorme quantité d'échantillons a été analysée grâce à la nouvelle technologie de mesure des isotopes de l'eau par un spectromètre laser (LWIA) récemment installé à l'Université de Stockholm dans le département de géochimie.

Pour valider les résultats provenant du LWIA, une attention particulière a été accordée dans cette étude au fonctionnement de celui-ci. Nous avons mis en place une méthode et un algorithme de traitement des données brutes permettant de parer les différentes sources d'erreurs de l'instrument. Nous avons détecté que la précision, médiocre par rapport au spectromètre de masse mais acceptable pour la plupart des études, est provoquée par une instabilité des mesures sur une longue séquence. Cette étude de lancement donne des pistes pour l'amélioration de la méthode énoncée par IAEA (IAEA 2009) et un ordre de grandeur de la précision pour notre étude (0.27‰ pour $\delta_{O^{18}}$ et 1.2‰ pour δ_D).

Une concentration importante de carottes de neige autour de la latitude 63°N a permis une très bonne résolution est-ouest du signal isotopique dans les précipitations pour la saison hivernale. Ces résultats mesurés montrent pour la première fois l'effet des précipitations provenant de l'Atlantique sur le signal isotopique par le phénomène de distillation de Rayleigh. Un modèle climatique introduisant les isotopes (REMOiso,) a permis de détecter l'index NAO exceptionnellement négatif de cette année, grâce à une comparaison avec les sorties de ce modèle sur 40 ans.

La stratification des carottes a permis de démontrer l'homogénéité de la couverture de neige localement, mais aussi sur un rayon de plusieurs dizaines de kilomètres. Pour le site de Vindeln, la stratification a permis de dater les événements à partir de données météorologiques, permettant ainsi de donner les valeurs $\delta_{O^{18}}$ et δ_D pour chaque événement neigeux détectable. Cette méthode de datation semble bien fonctionner lorsque le manteau neigeux n'est pas perturbé par la fonte, et devrait pouvoir être répété pour les autres sites ou d'autres études futures utilisant le même protocole.

Finalement, cette étude est une contribution pour enregistrer, commenter et comprendre cet hiver inhabituel. De plus, l'application de cette nouvelle méthode intéresse de nombreux domaines en science : la quantification et la datation d'autres éléments dans les précipitations hivernales, la validation des sorties de modèles climatiques couplés avec les isotopes, l'ajout de données entrantes pour les modèles hydrologiques utilisant les isotopes. Et à terme, pour la paléoclimatologie, une meilleure interprétation des proxys $\delta_{O^{18}}$ et δ_D , notamment des carottes sédimentaires lacustres, qui nécessitent une compréhension pointue sur l'ensemble du processus hydrologique faisant intervenir les isotopes de l'eau.