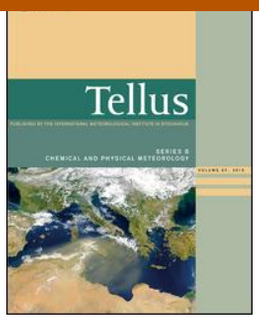

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Deuterium–hydrogen ratios, electrical conductivity and nitrate for high-resolution dating of polar ice cores

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ABSTRACT

In order to support the very high time resolution required to observe short-term variations in nitrates and all other ions represented by electrical conductivity in polar ice, a Fourier transform infrared spectrometer was developed for measurement of deuterium concentration in ice samples, as an additional support for the timescale of ultra-high resolution. The portable instrument provided the possibility to measure deuterium concentration on exactly the same samples as used for measuring nitrate concentrations and liquid electrical conductivity, thus verifying that the original dating of the annual variations in nitrate was correct. We present basic information about how the high-resolution data were obtained and discuss their reliability and significance.

Keywords: deuterium, nitrate, ice core, high-resolution dating

1. Introduction

This article presents an early use of a Fourier transform infrared (FTIR) spectrometer developed to determine the deuterium concentrations in water samples from arctic areas, where the deuterium is highly depleted. The D/H measurements were anticipated to be included in our extensive work to detect variations of ultra-high-resolution nitrates deposited in ice in Greenland and Antarctica.

In the original work (Dreschhoff and Zeller, 1994; Zeller and Dreschhoff, 1995), we analysed a core (GISP2 H) mainly for nitrate with the additional aid of liquid electrical conductivity giving specific time-markers due to known volcanic eruptions. The nitrate themselves proved to show an annual variation, therefore dating of the core and events was made possible and assisted with electrical conductivity measured with a separate instrument, however within the same melt-stream, i.e. both measurements were done on the same small sample. The idea of further proving that the counting of annual variations with nitrate and conductivity was indeed correct, we were able to add the FTIR instrument to determine D/H which is known to provide the signal of annual variations.

The motivation to add the D/H measurements was to enhance the dating and time resolution in snow deposition records based on annual temperature variations. A combined record was produced spanning over several years of original data records of nitrate and liquid electrical conductivity, that allowed very high resolution along the ice core and therefore interpreting some of the variations in nitrate due to solar proton events with high confidence. Such an assignment of years was tightly controlled by signatures of well-known volcanic eruptions along the entire ice-core. Furthermore, the objective was to achieve a very high accuracy of measurement by doing all separate measurements simultaneously on exactly the same samples of very fresh core. All analytical instruments were therefore designed to be taken into the field. A detailed description of experimental procedures, i.e. sampling along the core and data acquisition are provided in the work by Dreschhoff and Zeller (1994).

Similar detailed work had never been done before. More often arguments against a need for such labour-intensive investigations have however failed because in most cases of using old core, core from disadvantaged locations (far outside of the high polar plateau with

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precipitation from the polar stratosphere), or core segments only estimating mostly to be in the correct time zone on the core to analyse for specific events, and therefore, have not been able to reach the high resolution needed (Wolff et al., 2008, 2012; Smart et al., 2014). However, it is shown, if the true effort is being made to accomplish high-resolution measurements, some success has been reported for very deep core segments (Mayewski et al., 1993; Melott et al., 2010). Furthermore, for very long-term deep ice-core results the dating was supported by oxygen isotope measurements (Mayewski et al., 1996; Wolff et al., 2010).

The article is not meant, by introducing FTIR, to replace other and current multiple instrumental techniques used by the ice-core community. In fact, the study is to show that the original dating (Dreschhoff and Zeller, 1994) used by annual variations in nitrate together with the detailed signal provided by liquid electrical conductivity was correct, so that it could be used to identify very short-term signals superimposed on annual variations. More detailed information on the FTIR spectrometer used and results obtained is given in the work by Dreschhoff and Laird (2000).

2. Deuterium concentrations in natural water and ice

2.1. General introduction

Faure (1977) reports for the two stable isotopes of water and their abundance in the hydrosphere to be

$$^{1}\mathrm{H} = 99.985\% \text{ and } ^{2}\mathrm{H} = \mathrm{D} = 0.015\%.$$

Usually, the concentrations of deuterium are measured as ratios of D/H in a mass spectrometer and are expressed in units of parts per million (ppm) of deuterium in comparison to hydrogen, or they are expressed in terms of per mil (‰) deviation of the isotope ratio from a standard. The standard reference in general use is an arbitrary point of reference called SMOW (Standard Mean Ocean Water). The data are expressed as δD defined by

$$\delta D = \frac{R - R_{\mathrm{SMOW}}}{R_{\mathrm{SMOW}}} \times 10^{3}‰, \quad (1)$$

where $R = \mathrm{D/H}$.

Consequently, for reporting the isotopic composition of hydrogen in terms of differences of D/H ratios relative to SMOW, negative values of δD indicate depletion of a sample in D relative to SMOW.

2.2. Deuterium in polar snow, firn and ice

Given the assumption that the D/H parameter reflects temperature at the time of snow formation, this method provides an indicator for mean annual surface temperatures, and high-resolution measurements allow the annual signal to be used for dating ice cores (Dansgaard, 1964). Some realistic δD values for Greenland and Antarctica for summer and winter snow layers, where the difference between summer high and winter low values are also depth dependent are listed below:

- In Greenland, the upper 5–8 m of the GISP2 core shows δD values between approximately –220 to –320‰ (Barlow, 1994). This means they are depleted in deuterium isotope relative to SMOW.
- In Antarctica, on the Ross Ice Shelf, the upper 13 m of firn shows maximum variations with δD values roughly between –200‰ and –280‰ (Palais et al., 1983). The δD values for summer and winter snow are much lower, however, at the South Pole, where near the surface the seasonal δD values ranges from about –300‰ to –450‰ as reported by Jouzel et al. (1979). At greater depth near about 20 m the variability decreases by almost one half (Jouzel et al., 1983).

The mass spectrometer δD data reported are usually measured with a high precision typically of the order of 2‰. Although, the high precision of mass spectrometry could not at that time easily be reached with IR-spectrometry even under optimum conditions, this evaluation shows that within limits the resolution allowed one to distinguish a seasonal signal. In addition, if such a signal can be delineated in the field, particularly for any of the firn or ice core samples, the advantages have been pointed out above and can offset the disadvantage of lower resolution.

3. FTIR – apparatus description

3.1. Bomem, Michelson-type spectrometer

Deuterium has been analysed by infrared (IR) spectrometry as early as several decades ago (Thornton and Condon, 1950), however, we were able to reach detection limits in the lower range combined with relatively high precision through the introduction of FTIR or Fourier transform infrared technology with its associated software.

The FTIR spectrometer used was a MB-100 Michelson-type spectrometer manufactured by Bomem. The spectrometer was a self-contained unit consisting of a sample compartment and a sealed interferometer compartment. Of particular interest for field operations was

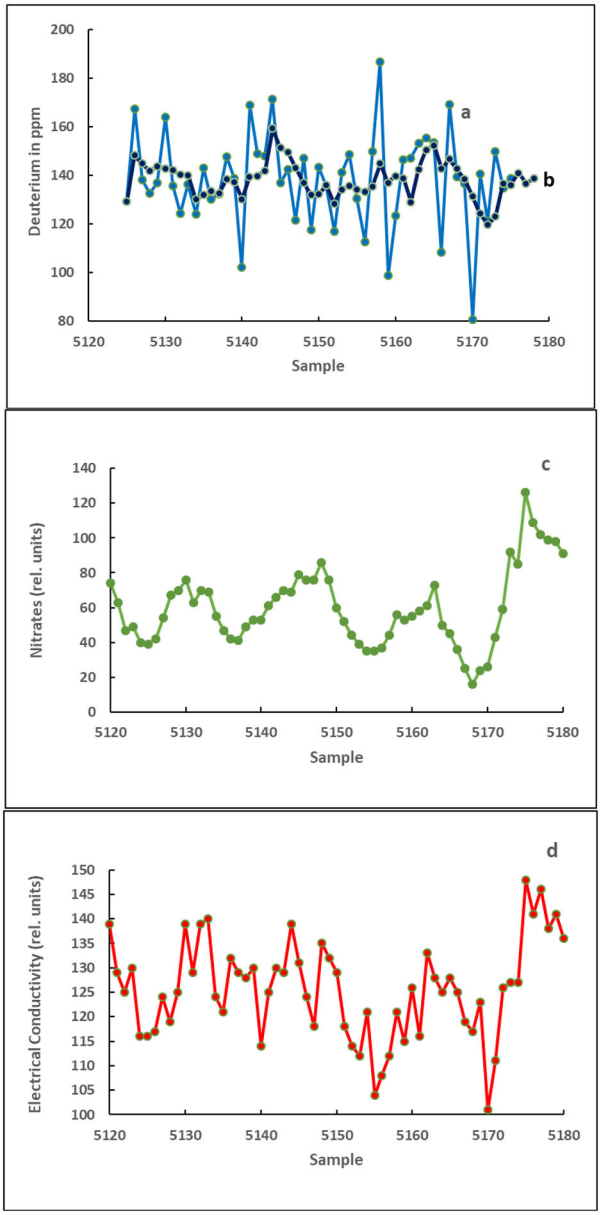

Fig. 1. The raw data of D/H as deuterium concentrations in ppm are plotted in (a). Superimposed on the D/H data is the three-point moving average (b). Added in the figure are the nitrate concentrations (c) and liquid electrical conductivity (d). All data sets were determined on exactly the same samples. This section of core (sample nos. 5120–5180) represents a depth of about 80.32–81.32 m of a 122-m long core and a total of 7776 samples (Dreschhoff and Zeller, 1994).

the feature of very high stability, permanent alignment and substantial immunity to vibration and variations in temperature. The interferometer was designed for long maintenance free operation. A crucial feature was the software designed by Bomem for optimum operation of the system. The general software incorporated data acquisition, fast Fourier transform (FFT) calculations, baseline corrections, spectral subtractions and spectral archiving. This software was integrated in a customised software analysis package for the specialised application for extremely low D/H ratios as encountered in the stratigraphic layers of polar snow and ice. Specifically, a K-Matrix quantitative method named 'D_2O cal 1' was generated for the calibration for measurement of D_2O. The spectrometric precision on measurements of the D_2O concentration was 2 ppm standard deviation for consecutive measurements on the same aliquot of a D_2O sample, with the cell in the sample holder (Leblanc, 1993). The analysis was simple and rapid and as many as 50 samples per day could be analysed. The system featured built-in diagnostics, i.e. an automatic system self-check at power on. The power requirements are 115/230 V AC, 50/60 Hz, 140 W maximum, being typically 75 W after warm-up. The total weight without the computer was 43 kg. The sample compartment was enclosed in a purge cover provided with an access door. It contained mirrors to channel infrared radiation to the sample position and to the detector. The instrument compartment contained a stabilised infrared light source, the Michelson interferometer, an infrared-transmitting 'beam-splitter,' a Helium–Neon laser for measurement of scan position, power supplies and electronic assemblies. The cast aluminium compartment was sealed to prevent the entry of dust and moist air, which could erode the beam-splitter.

One of the main features of the Bomem instrument was that the mechanical design of the MB series Michelson interferometer allowed the system to be insensitive to orientation and linear acceleration such as common vibrations (Lamarre and Baudais, 1990). It can be operated in environments having substantial vibrations such as in some field operations in Antarctica. The moving scan mechanism was based on the combination of a frictionless flex pivot bearing with a near frictionless scan motor and provided a drive mechanism and resultant scanning operation that was smooth, reliable and dependable over long periods of time. As a matter of fact, the lifetime of the pivot was virtually infinite. Furthermore, this interferometer design did not require optimising adjustments, it was permanently aligned.

4. Results of the study

First, measurements of D/H were made on very small samples of approximately one to a few millilitres, and the results showed that the method could be used to determine (a) long-term changes in deuterium abundance relative to hydrogen, and (b) a seasonal variation superimposed on any longer-term changes. With the system not being automated it nevertheless was capable of

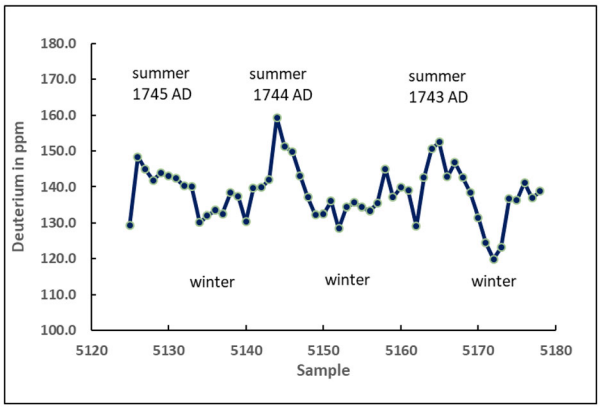

Fig. 2. The deuterium concentration data are plotted after applying a simple smoothing function (three-point moving average). The assignment of the years is indicated in the plot and is determined from dating the complete core from the surface to the depth of 122 m.

making about 50 analyses per day. Each measurement involved the comparison of two spectra, a reference spectrum and the absorbance spectrum of the sample. As reference, pure deuterium depleted water (natural abundance $\times$ 10^{-2}) was used, which is produced by the Aldrich Chemical Company. A series of tests were run using de-ionised (HPLC-grade) water as sample. By measuring more than ten sets of 3–25 samples in each set, the combination of instrumental error and variation in results between injected samples resulted in a precision of measurement of about ±10% (157.0 ± 15.7 ppm) for the deuterium concentrations. These measurements were run without the optical bandpass filter, which transmits only a narrow band of wavelengths or between 2882 and 2020 cm^{-1}. On the other hand, when adding the optical filter to the system the measurement of the natural abundance of deuterium in the water (HPLC) samples was reduced to ±3.8% or 157.0 ± 6.1 ppm.

The next step was to measure a series of samples, which were known to represent consecutive data points of seasonal variation for a total time period of more than three years. The samples were obtained from the GISP2 H-core in 15 mm increments (Dreschhoff and Zeller, 1994), each sample representing a time resolution of about one month.

The results are shown in Fig. 1 as raw data (Fig. 1a) together with corresponding nitrate (Fig. 1c) and electrical conductivity (Fig. 1d). In addition, the D/H data are plotted in Fig. 1b and Fig. 2 after applying a simple smoothing function (three-point moving average). Furthermore, in Fig. 2 the individual years are clearly indicated, although an uncertainty would arise near sample number 5158, which might be counted as an additional, but very short year. However, by comparing the data with the additional data series in Fig. 1c and d it becomes clear that this area of uncertainty can be easily resolved. We want to emphasise that all data sets in Fig. 1 are determined on exactly the same samples.

If we compare Fig. 1b and c, the seasonal variation is clearly indicated. This variation closely coincides with the basic winter lows and summer highs known not only from the nitrate profile illustrated in Fig. 1c but also from electrical conductivity in Fig. 1d, which frequently can serve also as a dating tool with annual resolution along an ice-core.

Considering the requirements for resolving a seasonal signal, the FTIR method was applicable. It was suggested (Palais, pers. com.) that the range of variation from summer to winter peaks in δD in West Antarctic snow is from about –160‰ to –260‰ compared to SMOW, and a precision of at least 10‰–15‰ is needed for the detection of the seasonal variation. This precision was in the range of the FTIR spectrometer used.

5. Discussion

Today's spectrometers like the one produced by Picarro, Inc. (www.picarro.com) based on a patented cavity ring-down spectroscopy (CRDS) technology provides clearly better precision and can, thanks to modern computer technology, run samples automatically with a high throughput (see also e.g. Litvak et al., 2018, for more references).

We want to emphasise that in our case the purpose was not related to climate studies as e.g. Mayewski et al. (1996) and Wolff et al. (2010), but simply to show that the combination of nitrate–liquid electrical conductivity measurements are useable for annual dating of an ice-core. The FTIR spectrometer described earlier was made available at an early stage of optical isotope spectrometers. But the possibility to include D/H measurements in the ice core studies, thanks to the early instrument developed, was extremely helpful and important when tracing the nitrate concentration in ice cores at very high time resolution. The ability to follow the annual variation in all three parameters provides a good quality control of the high-resolution data obtained from the whole record (122 m; 7776 samples) (Dreschhoff and Zeller, 1994). This is required when one wants to observe short-term signals and we want to underline the good correlation between the three records seen for the period shown in Fig. 1.

Any superposition of short-term (<1 year) fallout of stratospheric constituents as nitrate ions on such a seasonal/yearly signal can provide an active part of space climate studies (see Kilpua et al., 2015), beside tracers such as cosmogenic isotopes (^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl, etc.) (Mekhaldi et al., 2015; Sukhodolov et al., 2017 and

references there in). ^{10}Be has for a long time been recovered from ice cores collected in Antarctica and Greenland (Beer et al., 1990) as have been nitrate-ion.

Furthermore, study of these sudden short impacts on earth's atmosphere are traced not only in ice but also in tree rings (Hambaryan and Neuhäuser, 2013; Jull et al., 2014; Dee et al., 2016). Recently, Uusitalo et al. (2018) used ^{14}C in Arctic tree rings to study the solar superstorm of AD 774 and was able to show that it most probably occurred during the spring of that year.

Disclosure statement

No potential conflict of interest was reported by the authors.

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