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High resolution measurements of carbon monoxide along a late Holocene Greenland ice core: evidence for in-situ production

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Abstract

We present high-resolution measurements of carbon monoxide (CO) concentrations from continuous analysis of a shallow ice core from the North Greenland Eemian Ice Drilling project (NEEM-2011-S1). An Optical Feedback – Cavity Enhanced Absorption Spectrometer (OF-CEAS) was coupled to a continuous melter system during a 4-week laboratory-based measurement campaign. This analytical setup generates highly stable measurements of CO concentrations with an external precision of 7.8 ppbv (1 sigma) based on a comparison of replicate cores. The NEEM-2011-S1 CO record spans 1800 yr and exhibits highly variable concentrations at the scale of annual layers, ranging from 75 to 1327 ppbv. The most recent section of this record (i.e. since 1700 AD) agrees with existing discrete CO measurements from the Eurocore ice core and the deep NEEM firn. However, it is difficult to interpret in terms of atmospheric CO variation due to high frequency, high amplitude spikes in the data. 68% of the elevated CO spikes are observed in ice layers enriched with pyrogenic aerosols. Such aerosols, originating from boreal biomass burning emissions, contain organic compounds, which can be oxidized or photodissociated to produce CO in-situ. We suggest that elevated CO concentration features could present a new integrative proxy for past biomass burning history. Furthermore, the NEEM-2011-S1 record reveals an increase in baseline CO level prior to 1700 AD (129 m depth), with the concentration remaining high even for ice layers depleted in dissolved organic carbon (DOC). Overall, the processes driving in-situ production of CO within the NEEM ice are complex and may involve multiple chemical pathways.

1 Introduction

Carbon monoxide (CO) is a reactive trace gas, which plays a central role in climate/atmospheric chemistry interactions. CO is the principal sink for the tropospheric hydroxyl radical (OH), the most important oxidant in Earth's atmosphere. Up to 70%

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of the OH radicals react with CO in the modern troposphere (Karlsdottir and Isak-
sen, 2000), thus impacting lifetimes of numerous atmospheric components such as
methane, non-methane hydrocarbons (NMHCs), and hydrofluorocarbons (HCFCs).
Oxidation of CO by OH in high nitrogen oxides (NO_x) conditions can also result in
significant production of tropospheric ozone (Crutzen, 1973). Since CO impacts the
atmospheric budgets of greenhouse gases such as methane (CH₄) and tropospheric
ozone, it has a significant indirect warming potential.

A complete understanding of the modern CO budget and its evolution in relation to
past climate variability and recent anthropogenic influences is thus required for climate-
chemistry models. Improving our understanding of the sensitivity of these models re-
quires their evaluations over a variety of past climatic conditions. Martinerie et al. (1995)
suggested that changes in the oxidative capacity of the atmosphere (i.e. the levels of
atmospheric OH radicals) were mainly driven by CO levels during pre-industrial times.
However, reliable records of past atmospheric CO at glacial-interglacial time scales
are lacking, thus introducing uncertainties in models investigating climate evolution be-
tween the last glacial period, the pre-industrial Holocene, and the modern era. Such
records would help, for example, to better assess the poorly constrained balance be-
tween changes in sources and sinks driving rises of atmospheric methane during past
glacial-interglacial transitions, as revealed by ice core records (e.g. Valdes et al., 2005).

The short lifetime of CO, combined with significant variability in spatial distribution
of its sources, result in large variations of atmospheric CO levels with latitude. The
present day annual mean CO concentrations over Summit (Greenland) and South Pole
(Antarctica) are ~ 120 ppbv and ~ 50 ppbv respectively (<http://www.esrl.noaa.gov/gmd/dv/data/>). The lifetime of CO is estimated to be in the range of 20–40 days in the tropics
and up to three months in polar areas (Duncan et al., 2007). Sources of CO are qual-
itatively known, but still poorly quantified. In-situ atmospheric production by methane
and VOCs oxidations (Volatile Organic Compounds, including isoprene and terpenes)
represents ~ 50% of the sources. Carbon monoxide is also directly emitted to the
atmosphere by biomass burning, fossil fuel combustion, and vegetation and ocean

degassing (Duncan et al., 2007). Systematic monitoring of atmospheric CO, initiated by NOAA in 1988, revealed a global decrease of tropospheric CO of ~ 0.5 ppbv yr⁻¹ between 1988 and 1996 (Novelli et al., 1998).

Ancient air preserved in glacial ice and firn is thus unique archive to reconstruct the past atmospheric CO record. The firn is the upper layer of an ice sheet where snow is densified and transformed into ice. A large amount of air can be sampled from the interconnected open pores. Mean ages of atmospheric gas increase with firn depth. CO has only been sampled in firn at a few Northern Hemisphere sites over the last decade, including Devon Island (Clark et al., 2007), Summit, NGRIP, and the North Greenland Eemian drilling site (NEEM) (Petrenko et al., 2012). While the Devon Island record was affected by in-situ production of CO, the three Greenland records allowed for a 60 yr reconstruction of atmospheric CO and revealed a peak of ~ 155 ppbv during the late 70s. Further isotopic measurements on the NEEM firn air explained this pattern by a change in CO emissions derived from fossil fuel combustion (Wang et al., 2012).

While firn air data provide a robust reconstruction of atmospheric CO in the Northern Hemisphere since 1950, the only datasets that extend beyond this date are from the pioneering studies on ice core samples by Haan et al. (1996) and Haan and Raynaud (1998). These studies found CO increased gradually from ~ 90 ppbv in 1850 AD to 110 ppbv in ~ 1950 AD and that CO levels were stable around ~ 90 ppbv from 1625 to 1850 AD. Air older than 1600 AD (i.e. samples collected deeper than 167 m) exhibited higher CO levels (100–180 ppbv) characterized by a strong variability and an underlying increase going back in time with parallel anomalies in the CO₂ record. This part of the Greenland record likely reflects in-situ CO production rather than an atmospheric signal. Several ice core and firn studies have also been conducted in Antarctica, allowing for temporal reconstructions of atmospheric CO at Southern latitudes (Haan and Raynaud, 1998; Ferretti et al., 2005; Assonov et al., 2007; Wang et al., 2010). Wang et al. (2010) widened our knowledge of the variability of the past biogeochemical CO cycle by measuring both mixing and isotopic ratios from Antarctic ice cores. They interpreted the records as reflecting important variations in biomass burning during the last

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650 yr including a decrease of 50 % in the 1600s. Wang et al. (2010) clearly demonstrate the potential of measuring CO in ice archives. However, due to the short CO lifetime, such Antarctic reconstructions are partially decoupled from Northern Hemisphere atmospheric CO history, and thus reliable Greenland CO records are needed.

Ice core CO concentrations are typically determined by gas chromatography using a mercuric oxide detector (Haan et al., 1996; Haan and Raynaud, 1998) or a mass spectrometer (Wang et al., 2010) combined with wet or dry extractions of the trapped gases from discrete pieces of ice (Ferretti et al., 2005). Such protocols are time consuming and result in limited time-resolution reconstructions. Such low resolution is not optimal for investigation of in-situ production processes: the number of discrete samples is usually limited, and a single measurement averages CO concentrations over a depth of typically 5 cm, while in-situ production could be limited to thinner ice layers.

In the framework of the recent NEEM (77.45° N, 51.06° W) drilling project, a new technique allowing for rapid and high resolution measurement of methane (CH₄) in ice cores was developed (Stowasser et al., 2012). Gas released from bubbles in the ice is continuously extracted and CH₄ levels are detected in real time using laser spectroscopy, while the liquid phase sample is directed to the continuous flow analysis setup for chemical analysis (Kaufmann et al., 2008; Bigler et al., 2011). This technique enabled the reconstruction of an atmospheric CH₄ record of unprecedented resolution spanning the last deglaciation and glaciations back to Marine Isotope Stage 5d in a single field season (i.e. 2.5 months) (Chappellaz et al., 2013).

In this study, we report the first CO measurements from an ice core based on the coupling of continuous extraction and laser spectrometry. CO was continuously measured on the 340 m long NEEM-2011-S1 ice core along with methane concentrations (Rhodes et al., 2013) and a suite of chemical species. The objective of this study was to reconstruct an atmospheric history for CO over the past 1800 yr, taking advantage of the high resolution measurements to (i) distinguish between depth sections impacted by in-situ CO production and sections preserving the atmospheric record, and (ii) to

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investigate in-situ produced CO as a new biogeochemical proxy for biomass burning intensity by comparing CO measurements with other chemical impurities.

2 Methods

2.1 NEEM-2011-S1 ice core drilling

5 The NEEM-2011-S1 ice core described in this study was drilled in northern Greenland to a depth of 410 m. The borehole location was 200 m from the main NEEM borehole (77.45° N, 51.06° W). Drill fluid (Estisol 240 and Coasol) was used to reduce strain during core drilling below 80 m depth. Two parallel sticks were cut from the ice core for continuous analysis (M and B cut, each 110 × 3.4 × 3.4 cm).

2.2 Detecting CO with OF-CEAS

10 Gas extracted from the ice core was measured with a laser spectrometer SARA developed at Laboratoire Interdisciplinaire de Physique (LIPhy, Grenoble, France) and based on Optical Feedback-Cavity Enhanced Absorption Spectroscopy (OF-CEAS, Morville et al., 2005; Romanini et al., 2006). Briefly, the OF-CEAS analyzer used here measures CO, CH₄, and H₂O by fitting the sample gas absorption spectrum obtained in the 2325.1–2325.5 nm wavelength range. The analyzer has a 12 cm³ cavity, which is maintained at 20 mbar to create an effective cavity volume of only 0.24 cm³ at STP. Even at the low gas flow rates from continuous ice core analysis (typically 1.5 sccm with our CFA setup) the theoretical sample transit time in the cavity remains low (10 s).
15
20 During this measurement campaign the rate of OF-CEAS spectrum acquisition was 6 Hz. Consequently, the concentration measurements are much faster than the transit time, and the results may be averaged. This SARA instrument is specifically adapted for ice core analysis where only limited volumes of gas are available. However, the CFA

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setup itself introduces a stronger signal smoothing compared to the time resolution of the SARA instrument (Sect. 2.4).

A filter with a grid size of 2 microns (ZUFR1, VICI AG, Switzerland) was connected on the gas line upstream of the SARA instrument to avoid dust particles entering the optical cavity and depositing on the high reflectivity mirrors. We did not observe any significant decrease in ringdown (RD) time during the campaign, with a RD value stable and $> 40 \mu\text{s}$ (i.e. an optical path length of $> 18 \text{ km}$).

The OF-CEAS analyzer was carefully calibrated before melting the NEEM-2011-S1 core (see SI). However, we identified a small CO contamination from the mass flow controller (MFC, 5850E, Brooks Instrument, Hatfield USA) used to regulate the standard gas flow provided to the laser spectrometer during calibration. Measurement series (10 min each) of gas standards 1 and 2 (Table 1) with a constant flow of 1.5 sccm showed an increase of 4 ± 1 ppbv of CO when controlled by the MFC, compared to a direct connection to the cylinder regulator. This contamination from the MFC should be independent from the composition of the standards.

2.3 Continuous flow analysis of the gas phase

2.3.1 System operation

Detailed description of the continuous gas flow analysis method and integration of the gas system into the continuous melter system at the Desert Research Institute (DRI) for the NEEM-2011-S1 analysis is provided in Stowasser et al. (2012) and Rhodes et al. (2013). Briefly, ice core sticks were melted at a mean rate of 6 cm min^{-1} and the water and gas bubble mixture was pumped via a debubbler and open split into a gas extraction unit. Here the gas was extracted by applying a depression across a gas-permeable membrane (MicroModule $0.5'' \times 1''$, G591, Membrana GmbH, Germany, internal volume 5.4 mL) and then dried by an nafion (PermaPure) dryer. After each run of $\sim 8 \text{ m}$ of ice core was completed, a 4-port valve underneath the melterhead was switched to provide a synthetic air-water (10 : 90) mixture to the gas analysis system.

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For this purpose, an in-house deionized (DI) water supply was degassed continuously by mixing it with ultra-pure N₂ and passing it through another gas permeable membrane module. M cut ice sticks were melted successively from bottom to top of the core. Selected B cut sticks were analyzed as replicates.

2.3.2 Loop modes: mixing gas standards and degassed water

The NEEM-2011-S1 methane record reported by Rhodes et al. (2013) was corrected for a ~7% loss of methane due to dissolution in the sample stream. The CH₄ loss was quantified by introducing a 10/90 mixture of synthetic air and DI degassed water (from an N₂-purged 2 L reservoir) into the system via a 4-port valve directly after the melterhead (see Fig. 1 in Rhodes et al., 2013). The air-water mixture followed the same path through the system as the ice core sample before being analyzed by the laser spectrometer. This sample pathway was called the “full loop”. Results from analysis of the full loop are used here in an attempt to quantify both solubility and contamination effects on CO levels (see Sect. 2.3.3).

A second pathway for introduction of synthetic standard gas called the “internal loop” involved a 50 : 50 gas standard/degassed water mixture generated inside the gas extraction unit and was used to isolate the continuous flow gas setup from the remainder of the DRI melter system. It aimed at keeping water all time in the extraction module and a constant gas flow in the OF-CEAS spectrometer, and at providing an evaluation of possible drifts of the extraction and analysis system aside from those caused by processes upstream in the CFA system.

2.3.3 Precision of CO analysis

Allan variance (Allan, 1966) evaluation was conducted for direct measurements of dry gas standard, as well as measurements on gas standard mixed with DI water in both internal loop and full loop modes (Fig. 1).

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A precision of 0.05 ppbv is reached at the optimal integration time of 6 min when dry gas is measured directly. Optimal integration time for measurements made in the internal and full loop modes are 44 and 5 s respectively, with corresponding precisions of 0.13 and 0.30 ppbv. Allan variance analysis reveals that the stability of the OF-CEAS analyzer is not the limiting factor when measuring the CO concentration along an ice core. Rather, drift and noise are introduced by the continuous melting system and gas extraction, although the precision is still satisfactory for our study.

Internal loop measurements also provide insights about the precision of the continuous CO analysis. The CO concentrations for standard 1 mixed with degassed DI water in the internal loop mode were 70.0 ± 5.9 ppbv (9 internal loop measurements of 10 min length each and distributed over the complete analytical campaign, Table 1). Relatively constant levels throughout the analytical campaign (8.4 % relative standard deviation (RSD)) indicate that our CO measurements are reproducible. However, they lie between 10–20 ppbv CO above the certified standard value, without accounting for possible decrease in CO concentrations due to dissolution. We concluded that a component of the gas extraction system was contaminating CO along the internal loop line.

External precision of the continuous CO measurements (i.e. including all sources of errors or bias) was investigated by melting replicate ice sticks on different days during the analytical campaign. More than ten 1 m long ice sticks from the B cut were melted for that purpose. Direct comparison of CO records from these B cut sticks with data collected along the M cut revealed an excellent repeatability of our measurements, at least for CO concentrations ranging 120–600 ppbv. Figure 2 reports a direct comparison of CO measured along 12 m of parallel B and M cuts, which were processed three days apart. A constant 5 cm offset has been applied on the B cut depth scale used on Fig. 2. This offset is within the uncertainty range of the NEEM-2011-S1 depth scaling (see Sect. 2.4.2), and this correction is supported by the excellent agreement between CO data collected along both cuts. CO concentrations measured on both cuts were averaged by binning over 9 cm long intervals (Fig. 2, inset) and show excellent

correlation ($r^2 = 0.91$) between averaged CO from cut B versus averaged CO from cut M. Such correlation demonstrates the good precision of our measurements.

CO concentrations over the 153–167 m depth section of the NEEM-2011-S1 core exhibit highly variable values, ranging 120–320 ppbv, and slopes reaching 14 ppbv cm^{-1} .

The patterns of large CO variability over small depth variations will be discussed in more details in Sect. 3. Figure 2 demonstrates that the analytical system replicates both the amplitude in CO spikes, and the highly dynamic signal. We calculate a standard deviation (SD) of 7.8 ppbv from the comparison of these two runs (SD calculated on the difference of CO concentrations from cuts M and B, over the 45.9 cm long intervals represented on the inset of Fig. 2). This can be considered as the external precision of the analytical system and demonstrates the good precision of our measurements.

2.3.4 Accuracy of CO analysis: an attempt for absolute calibration

Our analysis of external precision (see Sect. 2.3.3) suggests that the influence of both contamination from the analytical system and potential losses related to dissolution of CO in the liquid phase were systematic and remained stable throughout the analytical campaign. However, these effects need to be quantified if one wants to improve the accuracy of the continuous CO measurements in order to reconstruct absolute CO concentrations. We thus investigated the full loop mode (see Sect. 2.3.2) as a calibration method. CO concentrations reported in this section are presented as mean ± 1 standard deviations.

An ideal calibration curve plotting full loop measurements against those on dry gas would have a slope reflecting dissolution losses and an offset reflecting the degree of contamination from the system. The CO concentrations for standards 1 and 2 recorded in the full loop mode were with $104.3 \pm 7.9 \text{ ppbv}$ ($n = 19$) and 128.8 ± 6.1 ($n = 4$) ppbv respectively, significantly higher than those measured directly and via the internal loop (Table 1). Any decrease in CO related to dissolution was completely

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hidden by contamination artifacts. Surprisingly, the CO contamination appeared to be higher when measuring standard 1, preventing to establish a linear calibration curve with a reasonable slope from the full loop data. Instead, we conservatively combine all the full loop data from standards 1 and 2 to calculate the difference between full loop and expected CO concentrations. This calculation established a positive offset of 52 ± 26 ppbv. We previously established a positive offset of 4 ± 1 ppbv related to the MFC. Identical MFC were used for full loop and, thus, a similar offset was included in the 52 ± 26 ppbv value. To avoid taking into account twice the MFC contamination, all the CO data collected along the NEEM-2011-S1 core were corrected for a 48 ppbv constant offset. Note that this correction does not take into account any solubility effect, which should be proportional to the concentration, but the magnitude of any such effect would likely fall within the error on the correction already applied. Consequently, CO concentrations may be over-estimated for values well above standard 2 levels (95.4 ppbv). We did observe such high CO levels when measuring the NEEM-2011-S1 core. We suggest that the large variability in the correcting offset evaluated from full loop data (i.e. ± 25 ppbv) very likely reflects variable levels of contamination originating from additional pump, tubing, connectors, etc., which are not present in the sample pathway.

Calibrating the continuous gas analysis systems for CH₄ has been shown to be already challenging. At the NEEM camp, Stowasser et al. (2012) report an unexplained positive offset of 25 ppbv of CH₄ between calibrated continuous data and discrete samples. The principal shortcoming of the continuous measurement technique is probably the uncertainty on the absolute concentration and this is particularly true in the case of the highly contamination-sensitive CO measurement. The continuous, high resolution, CO record collected along the NEEM-2011-S1 ice core shows an excellent precision, but its accuracy would need to be improved through a better calibration method. Thus, we focus the following on a qualitative discussion of the NEEM-2011-S1 CO record, where the precise measurements allow trends to be discussed.

2.4 Data processing and depth scaling

The entire CO dataset collected along the NEEM-2011-S1 core was averaged with a 5 s window, i.e. a duration shorter than the sample transit time in the spectrometer cavity (see Sect. 2.2). CH₄ data from NEEM-2011-S1 were screened for ambient air contamination (Rhodes et al., 2013), and any time-series removed from the CH₄ dataset was also removed from the CO dataset. Sections of the CO record affected by water vapor in the cavity could not be corrected are not considered here.

Depth scaling of the CO data collected along the NEEM-2011-S1 core was achieved by using the start/stop times recorded during melting, and by assuming a constant melt rate for each 110 cm core section. We estimated daily the time delay between the end of ice core melting at the melter head and the response of the CO signal measured by the OF-CEAS spectrometer (2.6–4.3 min range). To do so, we allowed air from the cold room to enter the sampling line at the end of a melting run, which resulted in a clear, sharp methane peak measured on the OF-CEAS spectrometer. The uncertainty revealed by these estimates corresponds to a depth uncertainty of ± 6 cm (2σ) (equivalent to 0.3 yr in age).

Signal smoothing resulting from memory effects was calculated by performing a step test, i.e. a switch between two gas standards of different concentrations, following the methods of Stowasser et al. (2012) and Gkinis et al. (2011). Both CO and CH₄ step patterns were investigated. CO step analysis indicates that 5 min – equivalent to 30 cm of sample length – have to be removed from the start of each 8 m melting run so as to eliminate effects of sample mixing with gas standard in the system. CH₄ step analysis reported previously by Rhodes et al. (2013) indicated that 7 min of data, equivalent to 42 cm sample length, had to be removed from the start of each 8 m melting run so as to eliminate CH₄-related memory effect. CO and CH₄ data from the NEEM-2011-S1 core were processed together, and 7 min of data from both CH₄ (Rhodes et al., 2013) and CO (this study) were conservatively discarded from the start of each run. The maximum temporal resolution of the CFA system can be evaluated from the transfer

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function produced by the step test (e.g. Stowasser et al., 2012). At a 6 cm min^{-1} melt rate a periodic CO signal in the ice with a wavelength of 7 cm depth can still be detected, although it will be significantly dampened (Fig. S1).

Finally, the NEEM-2011-S1 ice age scale (Sigl et al., 2013) and the modern-day gas age-ice age difference (Δage) for NEEM ($182 \pm 3/-9$ yr, Buizert et al., 2012), considered as constant along the depth range investigated here, were used to generate the gas age scale.

2.5 Chemical analysis

Ice core sample were analyzed continuously by inductively coupled plasma mass spectrometry (ICP-MS) and by fluorimetry for a broad range of elements and chemical species during the analytical campaign. These analytical methods have been reported previously (McConnell et al., 2002, 2007; McConnell and Edwards, 2008). In this study, we specifically investigated refractory Black Carbon (rBC) and ammonium (NH_4^+). Selected ice samples were also measured for discrete chemical analysis at LGGE (Grenoble, France), including DOC, formaldehyde (HCHO), and NH_4^+ . The methods used for these analyses are described in a companion paper (Legrand et al., 2013a).

3 Results and discussion

3.1 In-situ production of CO along the NEEM-S1 core

The full CO record available from the NEEM-2011-S1 core is reported in Fig. 3 and plotted versus the mean gas age. CO levels reconstructed over the last 1800 yr exhibit elevated and highly variable values, ranging from 75 to 818 ppbv, and one event peaking beyond this range at 1327 ppbv in 1465 AD. We demonstrated an excellent reproducibility in CO measurements (see Sect. 2.3.3), thus these patterns cannot be explained by measurement artifacts. While abrupt CO spike patterns will be discussed

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in Sect. 3.1.2, a key question to address is whether an atmospheric signal can be extracted from the low frequency variability of the NEEM-2011-S1 record's baseline.

3.1.1 CO baseline levels

We identified the NEEM-2011-S1 CO baseline by considering only data lower than a cut-off value of running median $-0.5 \times \text{MAD}$, where the running median has a window of 15 yr, and MAD is the median absolute deviation. A window a 15 yr correspond to a length smaller than the FWHM of the CO age distribution at the NEEM close-off (Fig. S4 in Petrenko et al., 2012). Note that any window length between 10 and 20 yr produces very similar spike identification. MAD values were calculated separately for the 1680–1950 AD, the 1100–1680 AD, and the 250–1100 AD sections of the record to account for increasing variability in the CO data. The NEEM-2011-S1 CO record exhibits the highest baseline values at the deepest depths analyzed (272 ± 85 m between 280 and 430 AD, i.e. depths ranging from 379 to 409 m). A decrease of ~ 0.05 ppbv yr^{-1} in baseline CO from the bottom of the NEEM-2011-S1 core to a period of relatively stable and low-concentrations occurring between 1700 and 1840 AD can then be observed. Increasing CO concentrations between 900 and 1000 AD, and fast decrease in CO from 1100 to 1200 AD, suggest however a period of higher CO between 900 and 1200 AD, a feature superimposed on the monotonic decreasing trend described previously. Unfortunately, no data were collected from ice core sticks dated 1000–1100 AD due to analytical issues. Finally, baseline CO shows a rapid increase at a rate of 1 ppbv yr^{-1} from its minimum in 1840 AD to close-off depth (i.e. 78 m) where concentrations of ~ 140 ppbv are observed, in agreement with CO concentration measured in the deep firn air in 2008 (Fig. 3, inset).

Figure 3 also provides a direct comparison of the NEEM-S1-2011 and the Eurocore (Haan and Raynaud, 1998) records during the last millennium (i.e. 1200–1950 AD). Eurocore was drilled at Summit, Central Greenland (75.58° N, 37.54° W, elevation: 3240 m; mean annual temperature: -32° C). Before 1600 AD the Eurocore CO record exhibits elevated and variable CO levels (100–180 ppbv) related to in-situ production

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(Haan and Raynaud, 1998). The Eurocore CO is stable at ~ 90 ppbv and increases from 90 to 110 ppbv, respectively between 1600 and 1850 and between 1850 and 1950 AD. From 250 to 1680 AD baseline NEEM-2011-S1 CO concentrations are higher than those observed on the Eurocore core for the 1600–1850 AD period, and even higher than those reported recently by direct atmospheric monitoring conducted at remote northern latitudes (see Sect. 1). NEEM-2011-S1 CO levels before 1680 are also almost always higher than the value of ~ 158 ppbv, the peak in CO concentrations reconstructed over Greenland using three different firn air archives (Petrenko et al., 2012). Between 1680 and 1950, the agreement between NEEM-2011-S1 baseline and Eurocore CO records improves. Specifically, the mean NEEM-2011-S1 CO is 100 ± 16 ppbv and increases from ~ 90 to ~ 120 ppbv, respectively between 1600 and 1850 and between 1850 and 1950 AD. Thus, the NEEM-2011-S1 data reproduce the increasing trend in CO concentration revealed by the Eurocore data and starting in 1850 AD. The NEEM-2011-S1 record also reach in 1950, i.e. at the close-off depth, a level similar to the deepest firn sample collected at the NEEM site and analyzed for CO (~ 120 ppbv at 78 m depth, inset on Fig. 3). Thus, we cannot rule out that the most recent 300 yr section of the NEEM-2011-S1 CO record reflects genuine variation of the past atmospheric CO, specifically the 1850–1950 increase in concentration. However, the NEEM-2011-S1 data are still highly variable, with no stable baseline identifiable. If the in-situ production perturbations were only related to specific ice layers, one would expect to observe a continuous CO trend between these layers. Such trend would reflect the atmospheric CO history smoothed by firn processes (e.g. Spahni et al., 2003). This is not the case in our data, showing important variability also in the baseline values.

It is likely that almost all CO data, including minimum values, in the NEEM-2011-S1 record include a contribution of in-situ production. Thus, reconstruction of atmospheric CO histories from the NEEM-2011-S1 dataset would require a deconvolution from the processes involved in such CO production, a complex task which is not completed at this time (see Sect. 3.2). However, the monotonic decrease in CO baseline observed

from the bottom of the NEEM-2011-S1 to ~ 1700 AD show similar pattern than global biomass burning, which declined from 1 to 1750 AD (Marlon et al., 2008). Similarities between Eurocore and NEEM-2011-S1 trends over the last 300 yr also suggest that the NEEM-2011-S1 records may still reflect the general shape (if not the absolute values) of an atmospheric signal over this period. The NEEM-2011-S1 record does not allow disentangling in-situ produced CO from the atmospheric signal, and additional high resolution measurements of CO concentration on Greenlandic ice archives with different impurity compositions are warranted.

3.1.2 Abrupt CO spikes

Figure 3 reveals the occurrence of multiple spikes along the NEEM-2011-S1 CO record. Interestingly, the amplitude of these spikes increases with depth: the median absolute deviation is 17, 35, and 48 ppbv over the age intervals 1950–1680, 1680–1100, and 1100–250 AD, respectively. Similar increasing variability with depth in CO concentration has been reported previously by Haan et al. (1998) over the Eurocore archive. As for baseline determination (see Sect. 3.1.1), we identified the NEEM-2011-S1 CO spikes by considering only values above a cut off level of $2 \times \text{MAD}$ above the running median, where the running median has a window of 15 yr. The cut-off level thus increases with depth over the three age intervals described before.

This approach allowed us to identify 96 events of highly enhanced CO concentrations along the NEEM-2011-S1 record, with larger density of spikes observed at deeper depths. Maximum CO spike concentration observed were 120 ± 20 , 190 ± 36 , and 278 ± 57 ppbv ($\pm 1\sigma$, absolute concentrations) for the age intervals 1950–1680, 1680–1100, and 1100–250 AD respectively. However, these spikes have been smoothed by the CFA system, and real maximum CO in the NEEM-2011-S1 ice is expected to be higher. Our OF-CEAS spectrometer measured CH_4 simultaneously with CO along the NEEM-2011-S1 core. A direct comparison between continuous and discrete CH_4 measurement ratios has been reported by Rhodes et al. (2013). These authors demonstrated that continuous measurement could induce a dampening of 38 % of the CH_4

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concentrations: a specific methane spike of 67 ppb was measured with the CFA system, but discrete measurements resolved a 107 ppb spike. Assuming that similar smoothing affects CO spikes, maximum CO concentrations for the three age intervals described before would be ~ 193, ~ 306, and ~ 448 ppbv respectively.

As previously mentioned, excellent repeatability (Fig. 2) confirms that the CO spikes originate from the ice core itself, and do not involve production occurring in the sampling lines between the melter head and the CFA extraction box. The CO spikes are always extremely abrupt (i.e. occurring over 2 yr) and cannot be of atmospheric origin because high frequency signals are removed by firn smoothing processes (Spahni et al., 2003). Consequently, they have to be related in-situ production. These processes are limited to specific ice layers, suggesting that CO production is related to the chemical or micro-biological content of the ice. The horizontal extent of the ice regions showing enhanced CO cannot be quantified. However, similar CO signals (as well as methane spikes, see Rhodes et al., 2013) were recorded in parallel ice core sticks (M and B cuts, e.g. Fig. 2) encompassing a horizontal distance of 6.8 cm.

3.1.3 Is drilling fluid a source of CO contamination?

The question remains whether the CO patterns observed along the NEEM-2011-S1 core, i.e. both spikes and an elevated baseline, are related to contamination from the drilling fluid that is rich in organic compounds. The core was inspected for fractures in which drill fluid (Estisol 240 and Coasol) residue might have been present and obviously affected sections were removed prior to melting. However, the impact of drilling fluid on CO concentration within the ice cannot be ruled out completely. A test involving analysis of air inside the head-space of an Estisol 240 drill fluid container presumably saturated with vapour recorded excess CO concentrations of 700 ppbv. Interestingly, the same test recorded an excess CH₄ concentration of only 40 ppbv, confirming the more limited impact of drilling fluid on methane measurements (Rhodes et al., 2013). Such a test does not realistically simulate the potential pathways of sample contamination, i.e. fluid leaking in the ice during the drilling, and staying within the ice until

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analysis 5 months later. To further characterize how drilling fluid may have disturbed the CO record, we performed DOC analysis on a unique sample that was slightly cracked and observed DOC concentrations above 600 ppbC, an elevated value confirming contamination. DOC analysis shows very low background when measured in uncracked samples, with concentration typically lower than 20 ppbC (see Sect. 3.2.1).

An interesting feature on the NEEM-2011-S1 record is the higher CO baseline concentrations observed around 1000 AD, although some data are missing at these dates. This section of the core (240–295 m depth) showed many drilling cracks, and drilling fluid may have leaked in the ice. We thus suggest that this pattern is driven by drilling fluid contamination, and decided to not investigate more closely the CO pattern from 900 to 1200 AD, although this period coincides with the Middle Age climatic optimum, a period of warmer climate and change in fire regime (Marlon et al., 2008), where CO investigation would be particularly relevant. Note that these cracks did not alter the methane record preserved in the NEEM-2011-S1 core, as shown by the good agreement between NEEM-2011-S1 and GISP2 discrete methane data (Rhodes et al., 2013).

The physical quality of the core increased with depth. However, the frequency and magnitude of CO spikes were also observed to increase with depth. Excellent repeatability was observed in parallel M and B ice sticks (Fig. 2). We thus conclude that CO contamination induced by drilling fluid – baseline levels, and eventually spikes – only affected the 240–295 m depth section, and does not explain the variability observed at other depths along the NEEM-2011-S1 record.

3.2 Which processes are driving CO in-situ production?

3.2.1 Chemical processes

In order to characterize the chemical pathway driving in-situ CO production, we investigated co-variations of CO with NH_4^+ and rBC along the NEEM-2011-S1 core. Both have been identified as good tracers of biomass burning (Legrand et al., 1992; Savarino

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and if we exclude the seven events showing CO levels above 275 ppbv, there is a clear lack of dependency between these variables (Fig. 5).

We thus hypothesize that multiple different processes are involved in the CO production within the NEEM-2011-S1 core. The main sources of available fuel in the Northern Hemisphere are Canadian and Russian boreal forests that supply pyrogenic aerosols transported to the Greenland ice sheet (Novelli et al., 2003). Oxidation of organics material produced in biomass burning plume, and later deposited to the Greenlandic ice cap, has been suggested to explain the elevated and variable CO concentrations along the Eurocore core (Haan and Raynaud, 1998). The chemistry of material reaching Greenland is related to fire conditions, although meteorological conditions encountered by plumes during their transport toward Greenland can also play a role (e.g. the efficiency of scavenging processes). Smoldering dominates in boreal forest fires (Lebel et al., 1991), but the complexity of the chemistry of biomass burning plumes is still poorly characterized (e.g. Mason et al., 2006). A good understanding of the chemical processes driving CO in-situ production along the NEEM-2011-S1 core would thus require a thorough investigation of the chemical composition of layers enriched by pyrogenic aerosols, and a better understanding of how such composition relates to CO enhancements observed.

As a first attempt to apply such methodology, we selected a core section (138.8–140.4 m depth) showing elevated NH_4^+ , i.e. enriched with pyrogenic aerosols, for measurements of an extended array of inorganic and organic compounds and fractions. As a reference, similar analyses were conducted on a deeper section (296.3–296.9 m depth, reported later as the “reference section”) showing low NH_4^+ , i.e. not impacted by impurities originating from biomass burning. These results are discussed in detail in a companion paper (Legrand et al., 2013a), we only report here discrete analysis of DOC, formaldehyde (HCHO) and NH_4^+ (Fig. 6).

The reference ice section, covering 296.3–296.9 m depth (blue in Fig. 6), exhibits a clear seasonal NH_4^+ pattern, with winter concentrations below 5 ppb, and summer concentrations in the range of 9–12 ppb. Such variations can be explained by seasonal

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emissions from soils and vegetation (Fuhrer et al., 1996) and are similar to present day observations at the Summit Greenland site (Dibb et al., 2007). DOC and HCHO concentrations do not show such seasonal trend, but rather quite low values averaging 17.9 ± 9.2 ppbC and 2.2 ± 0.5 ppb respectively. rBC ranges between $4\text{--}12$ ng g⁻¹, and CO is 230.7 ± 21.8 ppbv, i.e. a value slightly above the 224.1 ± 5.2 ppbv of the 15 yr running median over this depth interval. The pyrogenic aerosol-enriched layer located at 140.15 m depth (black in Fig. 6) shows clear spikes in both NH₄⁺ (maximum of 143 ppbv) and DOC (maximum of 116 ppbC). HCHO averages 2.8 ± 0.5 ppb over the investigated section, and rBC ranges between 4 and 16 ng g⁻¹. Finally, CO peaks at 184 ppbv, a value 84 ppbv above the 15 yr running median as calculated at this depth (Fig. 6). The 140.15 m depth layer shows CO levels two MAD above running median, and is thus defined as a spike. CO concentration is higher for the reference core section (ranging from 192 to 296 ppbv), but with values similar to the 15 yr running median at the corresponding depth (Fig. 6). Higher CO value for the reference section thus reflects increasing baseline with depth, and not localized CO spike.

A comparison of the organic content in both polar ice caps shows that the Greenland ice cores are enriched by organic aerosols released in major boreal forest fires during the last two millennia (Savarino and Legrand, 1998). As expected, biomass burning is also a source of organic compounds at the NEEM site (Fig. 6, see also Legrand et al., 2013a). Although a large fraction of water soluble and insoluble organic carbon may be lost at the surface during post-deposition processes (as reported at the central Greenland station of Summit by Hagler et al., 2007), the amount of DOC still available in the ice (> 100 ppbC) represents an important reservoir of carbon which can potentially be oxidized to carbon monoxide. 100 ppb in volume of CO in NEEM ice translates into 12.5 ppt in weight. Therefore the amount of DOC in ice is more than four orders of magnitude larger than the potential amount of CO. The oxidation processes involved are not identified yet, and a better characterization of the speciation of the organic content of the NEEM-2011-S1 ice is required. A first attempt to determine such speciation for the 140.15 m depth layer is reported by Legrand et al. (2013a), and reveals that 80 % of

layer where DOC concentration is above 100 ppbC. It is thus likely that oxidation of organic matter is not the only mechanism involved.

3.2.2 Comparison with CO record from an alpine core

Col du Dome (CDD) is an elevated (4250 m a.s.l.), mid-latitude site located in the vicinity of the Mont Blanc summit (France). We investigated CO, NH_4^+ , and DOC from ice cores drilled at CDD (cores C10, C11, and CDK; Table 2) to investigate if the in-situ CO production observed along the NEEM-2011-S1 core could occur as well in mid-latitude glaciers, and eventually to improve our understanding of these processes. 11 discrete samples were analyzed in 2001 from the C10 and C11 cores for CO concentrations, following the protocol of Haan et al. (1996). NH_4^+ and DOC were analyzed in the CDK core (Preunkert and Legrand, 2013) and reported as splined trends in Table 2 to account for uncertainties in relative depth scaling between CDK and C10/C11 cores respectively.

Two summertime and two wintertime ice layers were identified using NH_4^+ , and were analyzed for CO (Table 2). We specifically investigated winter 1975 and summer 1976. CO concentrations in summer layers were about one order of magnitude higher compared to winter layers, with summer levels always above 1000 ppbv, and winter layer in the range of 300–500 ppbv. Along the 340 m long NEEM-2011-S1 core, spanning the last 1800 yr and continuously analyzed, only 11 CO spikes reaching concentrations above 500 ppbv were identified, and only one event showed CO above 1000 ppbv. NEEM-2011-S1 CO concentrations as reported in Fig. 3 may be lower than actual levels of the NEEM-2011-S1 core because of (i) the smoothing induced by the CFA system (see Sect. 2.4), and (ii) the lack for an absolute calibration (see Sect. 2.3.3). However, the in-situ production of CO is clearly enhanced in the CDD ice (i.e. mid latitude, alpine) compare to the NEEM ice (i.e. Greenland). These high CO levels in the CDD ice were observed only ~ 15 m below the close-off depth. We suggest that slow kinetic processes may build up CO with depth in the NEEM ice. In-situ production at CDD happens much faster.

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The reason for higher production of CO at CDD may include surface melting and percolation, although refrozen layers and melt water percolation within CDD ice cores occurs only in summer and is limited to a few centimeters, i.e. corresponding to the accumulation equivalent of a few weeks (Preunkert et al., 2000, and references therein).

5 Therefore liquid-phase chemical production of CO may occur, and explain a larger variability in CO concentrations in summer layers compared to winter layers. Another explanation may invoke the presence of much more organic material in the CDD ice compared to the NEEM ice. We found 116 ppbC of CO in a NEEM-2011-S1 layer affected by deposition of pyrogenic aerosols. DOC in CDD ice increases about a factor of
10 two between winter and summer, and its decadal averaged levels have doubled since the early 1900s century (Legrand et al., 2013b). Thus, one could argue than more CO can be produced if more DOC is available (i.e. just below the close-off), but similarly to the NEEM-2011-S1 record we expect more CO at deeper levels considering that CO in-situ production is driven by slow kinetic processes. Overall, these data confirm that
15 CO in-situ production is not limited to Greenlandic archives, and can be enhanced in middle-latitude glaciers, but more analysis is required for a final conclusion.

4 Conclusions

For the first time, a high resolution, continuous profile, of carbon monoxide concentrations has been measured along a 340 m long ice core, the NEEM-2011-S1 archive. The
20 measurements along the complete ice core have been carried out in only few weeks by coupling an OF-CEAS laser spectrometer with a continuous melting system. We demonstrate the good precision of this continuous CO analysis, with an external precision of 7.8 ppbv based on a comparison of replicate CFA slices. However, the accuracy needs to be improved by the optimization of our calibration methods.

25 The NEEM-2011-S1 CO record exhibits concentrations ranging from 75 to 1327 ppbv, thus too high and too variable to be interpreted as changes in atmospheric CO. The concentrations reconstructed over the period spanning 1650–1950 AD,

however, agree with CO signals retrieved from the discontinuous Eurocore CO profile (Haan and Raynaud, 1998) and the deep firn samples collected at the NEEM camp in 2008 (Petrenko et al., 2012). The good reproducibility obtained from parallel ice sticks demonstrates that the NEEM-2011-S1 highly variable CO patterns do exist in the ice itself, and are not measurement artifacts.

68% of the elevated CO spikes along the NEEM-2011-S1 core were observed in thin ice layers enriched with the pyrogenic aerosols rBC and NH_4^+ . Such aerosols, originating from boreal biomass burning emissions, contain an important organic fraction. Oxidation, eventually photo-induced dissociation, of organic compounds initially enclosed in the ice may produce CO in-situ, resulting in the elevated CO spikes. Thus, our study highlights the link between biomass burning events and in-situ produced CO in a Greenlandic ice core. This suggests a new proxy opportunity to investigate past fire history. The NEEM-2011-S1 record also reveals an increase with depth in minimum (not spiked) CO levels, with the baseline level remaining high for ice layers depleted of DOC. Although oxidation of organic matter is a likely mechanism for CO in-situ production, it is probably not the only mechanism involved. For instance, microbiological processes also need to be investigated more closely. Notably, high resolution, non-destructive, laser-induced scanning of chlorophyll and tryptophan fluorescence signal (e.g. Rohde et al., 2008) have been used to signal the presence of microorganisms along the ice core. Such methodology could be coupled to CFA analysis, and might provide new insights. Our study highlights the complexity of the processes leading to in-situ production of CO in ice cores.

More archives from both Greenland and Antarctica should now be investigated following a similar approach, to reconstruct the past history of atmospheric carbon monoxide. Antarctic ice may contain an undisturbed atmospheric record of carbon monoxide, which is representative of the Southern Hemisphere. Therefore, investigating Greenland archives is necessary to document past atmospheric CO from Northern Hemisphere. We advocate prioritizing measurements at Greenland sites where accumulation rates are high. Thick winter layers with low concentrations of organic

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precursors would result in minimal in-situ CO production. Coupled with a suite of chemical analysis, such records should enable disentangling in-situ produced CO from the atmospheric signal preserved in the ice.

Supplementary material related to this article is available online at:
<http://www.clim-past-discuss.net/9/2817/2013/cpd-9-2817-2013-supplement.pdf>.

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Table 1. CO concentrations of synthetic air standards and mean values of measurements conducted on dry gas introduced via the internal loop and via the full loop. Each value is the mean of several repeated measurements ($n = 2$ – 19) conducted throughout the analytical campaign, where each individual measurement has an integration time of 10 minutes. The stated uncertainty is 1 standard deviation. Synthetic air standards were calibrated by the NOAA GMD Carbon Cycle Group, and are reported on the NOAA/WMO 2004 scale.

	NOAA certified	Internal Loop	Full Loop
Standard 1	50.2 ± 0.7	70.0 ± 5.9 ($n = 9$)	104.3 ± 7.9 ($n = 19$)
Standard 2	95.4 ± 0.9	106.0 ± 3.5 ($n = 2$)	128.8 ± 6.1 ($n = 4$)

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Table 2. CO concentration measured at 11 depths in the C10 and C11 Col du Dome cores. DOC and NH_4^+ were measured in the CDK core, also drilled at Col du Dome. We report splined NH_4^+ and DOC data according to Preunkert and Legrand (2013), to represent seasonal averages. Dating of the C10, C11, and CDK cores has been reported by Preunkert et al. (2000) and Legrand et al. (2007) respectively.

Core	Depth (m)	Ice Age (AD)	CO (ppb)	NH_4^+ (ppb) spline	DOC (ppbC) spline	Season
C10	69.0	1976	1063 ± 16			
C10	73.15	1976	1196 ± 25			
C10	73.20	1976	3790 ± 7	147	210	Summer
C10	73.27	1976	3463 ± 130			
C11	109.3	1939–1947	3801 ± 76	69	95	
C10	71.2	1975/1976	377 ± 11	78	86	Winter
C10	72.1	1975/1976	473 ± 7	78	86	
C11	126.7	1912–1925	359 ± 9	40	44	
C11	99.9	1957	2003 ± 79	n.d.	n.d.	
C11	136.6	< 1910	1590 ± 42	n.d.	n.d.	n.d.
C11	137.5	< 1910	2616 ± 87	n.d.	n.d.	

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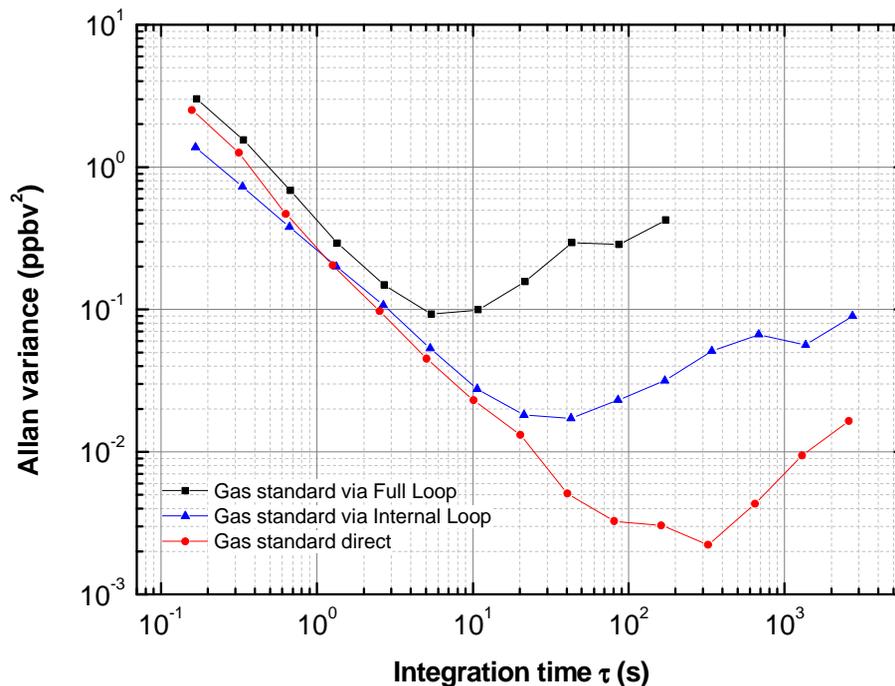


Fig. 1. Allan variance results for direct gas standard analyses conducted directly, and for standard gas introduced via both the internal and the full loops.

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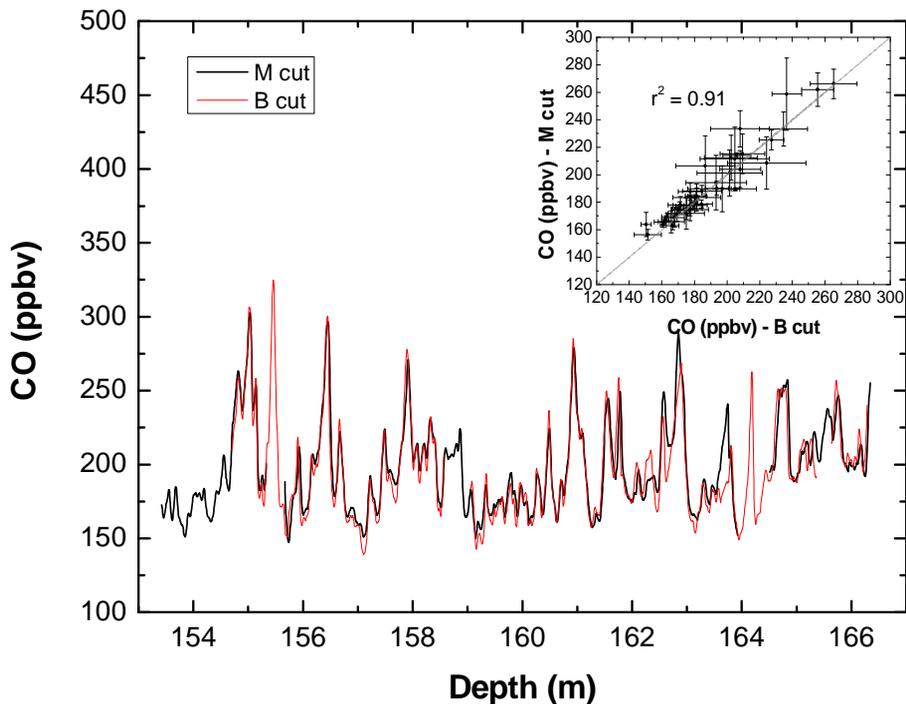


Fig. 2. Replicate measurements of CO concentrations (M cut in black, B cut in red) between depths of 154–167 m. Inset displays CO concentrations from cut M versus cut B, after averaging data over 9cm long depth intervals. Note that the B cut depth scale has been slightly adjusted (i.e. a 5 cm offset was applied), to perfectly line up both records.

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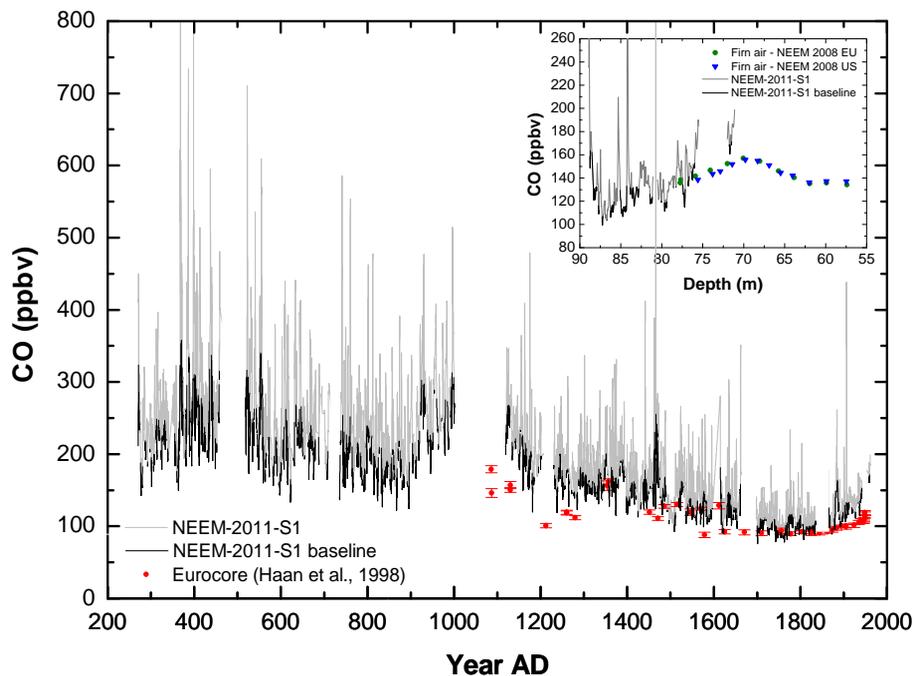


Fig. 3. NEEM-2011-S1 continuous CO record over the last 1800 yr (grey and dark). Signal baseline is defined by $0.5 \times \text{MAD} < 15$ yr running average (dark). CO concentrations from Eurocore (Summit, Central Greenland, red dots) are plotted for comparison. The Eurocore CO dating and corresponding uncertainties are discussed by Barnola et al. (1995). Inset displays CO from both NEEM-2011-S1 record and the 2008 NEEM firn air sampling (Petrenko et al., 2012) over the 55–90 m depth range.

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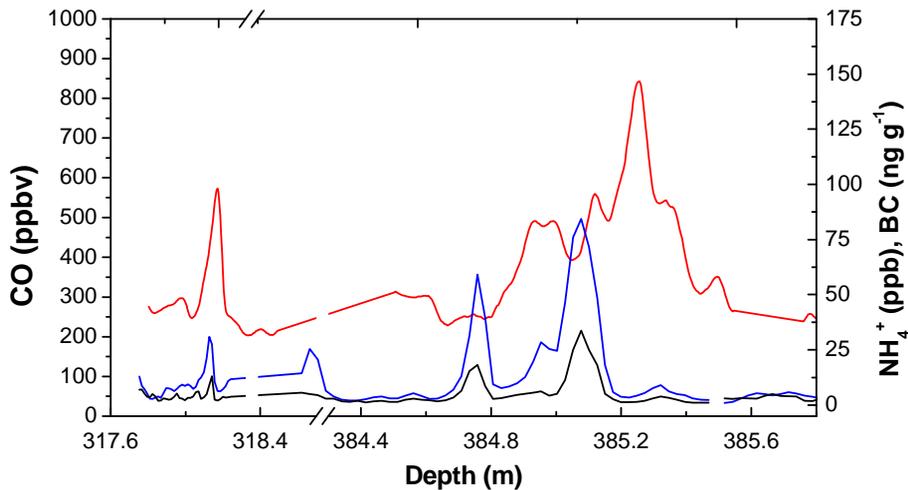


Fig. 4. CO, NH₄⁺ and rBC concentrations for two specific depth sections. The depth uncertainty is 6 cm.

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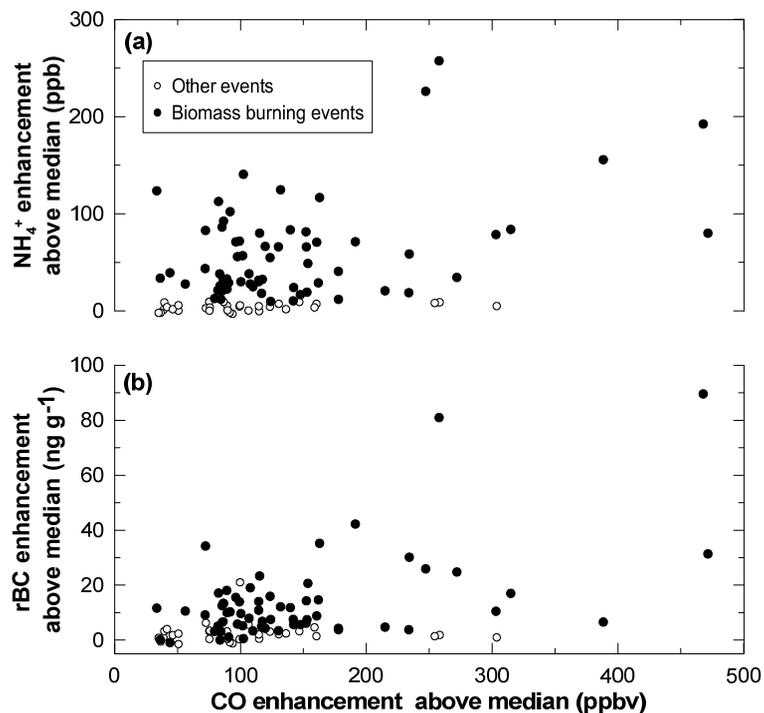


Fig. 5. CO concentration enhancements above median values for the 96 spikes selected along the NEEM-2011-S1 record, as a function of NH₄⁺ (a) and rBC (b) concentrations. Both NH₄⁺ and rBC are shown as enhancement levels above their corresponding median. Ice layers enriched with pyrogenic aerosols (closed circles) are identified when [NH₄⁺] > 18 ppbv (Savarino and Legrand, 1998).

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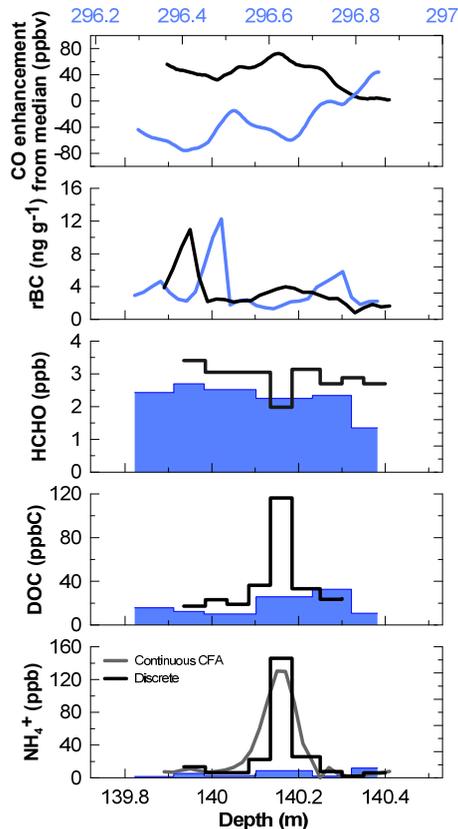


Fig. 6. CO enhancement from the 15yr running median, rBC, HCHO, DOC, and NH_4^+ over two selected layers of the NEEM-2011-S1 core: a pyrogenic aerosols enriched layer (139.9–140.4 m depth, black curves, bottom x-scale), and a pyrogenic aerosols free layer (296.3–296.9 m depth, blue filled curves, top x-scale). Both discrete and continuous (i.e. CFA based) NH_4^+ measurements are reported.

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