Radiocarbon analysis of stratospheric CO_2 retrieved from AirCore sampling.

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Abstract.

In this decade understanding the impact of human activities on climate has been one of the key issues of discussion globally. In that respect, the continuous rise of the concentration of greenhouse gases, e.g., CO_2, CH_4, etc. in the atmosphere, predominantly due to human activities requires continuous monitoring to understand the dynamics. Radiocarbon (^{14}C) is an important atmospheric tracer and one of the many used in the understanding of the global carbon budget, which includes the greenhouse gases CO_2 and CH_4. Measurement of radiocarbon in atmospheric CO_2 generally requires collection of large air samples (few liters) from which CO_2 is extracted and then the concentration of radiocarbon is determined using Accelerator Mass Spectrometry (AMS). However, the regular collection of air samples from the stratosphere, for example using aircraft and balloons, is prohibitively expensive.

Here we describe radiocarbon measurements in stratospheric CO_2 collected by the AirCore sampling method. AirCore is an innovative atmospheric sampling system, which comprises of a long tube descending from a high altitude with one end open and the other closed, and has been demonstrated to be a reliable, cost-effective sampling system for high-altitude profile (up to ≈ 30 km) measurements of CH_4 and CO_2. In Europe, AirCore measurements are being performed on a regular basis near Sodankylä (Northern Finland) since September 2013. Here we describe the analysis of samples from two such AirCore flights made there in July 2014, for determining the radiocarbon concentration in stratospheric CO_2. The two AirCore profiles were collected on consecutive days. The stratospheric part of the AirCore was divided into six sections, each containing ≈ 35 µg CO_2 (≈ 9.6 µgC). Each section was separately stored in a ¼ inch coiled stainless steel tubing (≈ 3m) for radiocarbon measurements. A small-volume extraction system was constructed which enabled ≈ 100% CO_2 extraction from the stratospheric air samples. Also, a new small-volume high-efficiency graphitization system was constructed for graphitization of these extracted CO_2 samples, which were later measured at the Groningen AMS facility. Since the stratospheric samples were very similar in mass, reference samples were also prepared in the same mass range to correct for contaminations. The results show that the $\Delta^{14}CO_2$ values for lower stratosphere up to about 18(± 1) km (first four samples from each profile) are very similar (10 ± 8‰) and represent the current tropospheric value. The next sample in each profile, corresponding to about 18(± 1)-22(± 2) km showed slight enrichment of 80 ± 20‰. The last section from one profile,

corresponding to altitudes above 22(± 2), also showed enhanced $\Delta^{14}CO_2$ value of 79.1 ± 30‰. The last section from the other profile was spoiled during preparation.

1 Introduction

The concentration of Greenhouse Gases (GHG), with carbon dioxide as the most prominent example, has been and still is increasing, predominantly due to emissions from fossil fuel combustion. The consequences in terms of climate change are certainly detrimental (IPCC, 2014a, b) if the rapid increase in GHG concentrations is not regulated and properly accounted for. This brings in the necessity for better understanding and quantification of the sources, reservoirs, sinks and the transport mechanisms involved.

Carbon dioxide is a naturally occurring greenhouse gas produced mainly through respiration by aerobic organisms and decay of organic materials. It is also the product of combustion of any carbon-containing compound. Carbon in carbon dioxide exists in the form of three naturally occurring isotopes, i.e., ^{12}C, ^{13}C, and ^{14}C. Radiocarbon (^{14}C) is the only naturally occurring radioactive isotope of carbon ($t_{\frac{1}{2}}$ = 5730 ± 40 years), which is continuously produced through the reaction of thermalized neutrons from cosmic radiations with ^{14}N in the upper atmosphere (Lingenfelter, 1963). The produced ^{14}C combines with oxygen to produce $^{14}CO_2$, which forms a trace component of atmospheric CO_2 (presently $^{14}CO_2/^{12}CO_2 \approx 1.2 \times 10^{-10}$ %). $^{14}CO_2$ is an important atmospheric tracer, which helps in the understanding of the levels of anthropogenic emissions from fossil fuels. This is due to the fact that fossil fuel is virtually radiocarbon-free, which upon combustion produces CO_2, also radiocarbon-free. This CO_2 from fossil fuel dilutes the atmospheric $^{14}CO_2$ concentration upon release.

The concentration of CO_2 throughout the atmosphere is roughly well-mixed, with an observed annual rise in recent years of $\approx$ 2 ppm/year (Hartmann et al., 2013). This rise in the concentration of CO_2 due to the burning of fossil fuels is at present the main cause for the decrease in the radiocarbon concentration in the atmospheric CO_2. Aircraft sampling of atmospheric CO_2 at various altitudes is regularly performed, which unfortunately only collects air samples up to upper troposphere/lower stratosphere (Sweeney et al., 2015;Machida et al., 2008;Brenninkmeijer et al., 2007;Brenninkmeijer et al., 1995). Although balloon based sampling has been demonstrated as a method for collecting stratospheric air for measurements of radiocarbon in stratospheric CO_2 (Ashenfelter et al., 1972;Nakamura et al., 1992;Nakamura et al., 1994;Hagemann et al., 1959), this method of sampling is extremely expensive and difficult to sustain for longer periods. Here we describe the use of the AirCore sampling method (Karion et al., 2010) as a viable tool for sampling stratospheric air for the measurements of radiocarbon in stratospheric CO_2. Although the sample sizes obtained through AirCore sampling are small (only $\approx$ 50 ml), they are just enough for performing quantitative radiocarbon measurements, with relatively good altitude resolution.

2.1 Sampling

Regular AirCore profiles of CO_2, CH_4, and CO have been made near Sodankylä (in Northern Finland, 67.4° N, 26.6° E) since September 2013 (Chen et al., In preparation). We have collected the stratospheric part of the AirCore samples for several selected AirCore flights using a stratospheric air sampler (Mrozek et al., In preparation). Briefly, the AirCore that has

5 been flown in Sodankylä comprises of a long coiled, thin-wall stainless steel tubing (≈ 100 m long, volume ≈ 1400 ml). The AirCore, before releasing with the help of a balloon, is first filled with a standard dry "fill-gas" with known CO_2, CH_4 and CO concentrations (CO_2 = 386.10 ± 0.09 ppm; CH_4 = 1880 ± 2 ppb; CO deliberately spiked to 7972 ± 5 ppb). The fill gas is a compressed air cylinder containing dry ambient air (sampled at Sodankylä, Finland) spiked with carbon monoxide. It should thus contain CO_2 with natural levels of radiocarbon. The accurate determination of the radiocarbon content in CO_2 of

10 the fill gas was initially not deemed essential for this work, and has thus not been performed. The AirCore is then released with one end open to atmosphere. As the AirCore travels higher in the atmosphere, the fill-gas inside the AirCore is evacuated due to the drop in pressure. During its descent through the atmosphere, the evacuated AirCore equilibrates with the ambient pressure and thereby the tube gradually fills itself with atmospheric air. The open end of the AirCore is then closed automatically upon landing, preserving the collected air column until analysis is performed, which is typically within

15 a few hours after the AirCore has landed.

For our goal, the AirCore, containing the vertical atmospheric profile, was connected to a Cavity Ring-Down Spectrometer (CRDS, Picarro Inc., CA model: G2401) for simultaneous measurements of the CO_2, CH_4 and CO concentrations. The sampling end of the AirCore was connected to a standard dry "push-gas" line, and the other end was connected to the CRDS analyzer. The sampled air column inside the AirCore was then "pushed" out with the push-gas, which is also the fill-gas, into

20 the CRDS analyzer. The exhaust from the CRDS analyzer was connected to a Stratospheric Air Sampler (SAS) (Mrozek et al., In preparation). The SAS built at the University of Groningen, similar to the one described in Mrozek et al., comprises of a series of six connected stainless steel tubing (Swagelok, od = 6.35 mm, id = 4.57 mm, ≈ 50 ml), with each section measuring 3 m. The tubing sections were joined by three port two way valves (Swagelok SS-43GXS4), which allows uninterrupted transfer of the AirCore content into the SAS and subsequent isolation of each section for a desired analysis

25 later. Each section in the SAS thus represented an integrated sample from a determinable altitude range. Each section contained ≈ 50 ml stratospheric air (at STP), with ≈ 35 μg CO_2 (≈ 9.6 μgC). CO_2 samples from each section of the SAS were later extracted and processed for ^{14}C measurements at the Centre for Isotope Research, (CIO), Groningen, using Accelerator Mass Spectrometry (AMS). The AMS facility at CIO is a 2.3 MeV Tandetron built by High Voltage Engineering Europa (Gottdang et al., 1995).

30 Several AirCore profiles were collected at Sodankylä during a campaign in July 2014, out of which two stratospheric air profiles were preserved for radiocarbon measurements of stratospheric CO_2 described in this work. Figure 1a shows the picture of an AirCore that was used during the sampling campaign. Since the AirCore is initially filled with a fill-gas before

release, there is a small fraction of the fill-gas still remaining in the AirCore, which is not evacuated completely. This leftover fraction of fill-gas contaminates the air from the highest sampled altitude. Fortunately, the impact on the samples from the highest altitude can be accurately corrected for when using fill gas with an enhanced CO of 7972 ± 5 ppb to label the mixing process (Chen et al., In preparation). These corrected atmospheric profiles of CO_2 (red, solid and dashed lines)

5   and CH_4 (blue, solid and dashed lines) from the two AirCore samplings are shown in Fig. 1b. The CO_2 profile is roughly well-mixed throughout the atmosphere, whereas the CH_4 concentration is rather constant in the troposphere and drops continuously with increasing altitude in the stratosphere, predominantly due to oxidation.

2.2 Extraction

Following the sample collection at Sodankylä, the SAS was brought back to Groningen for subsequent processing and

10   measurement. CO_2 from the air samples in the SAS was extracted using an extraction system (total volume ≈ 20 ml) as shown in Fig. 2a. The detachable CO_2 trap, made from Pyrex, has two flow-through freezing tubes submerged in a liquid air bath. Each section of the SAS is individually connected to the extraction system. The extraction system is first evacuated for approximately an hour and then the air from the SAS is slowly expanded, during which the CO_2 trap is submerged in liquid air. During this expansion of sample in the extraction system, a reference air (#1) is directed into the connected CRDS

15   analyzer (Picarro G2301) through a 3-port 2-way valve. Once the pressure in the extraction system stabilized, the air from the extraction unit is directed into the CRDS analyzer to determine the CH_4 and the remaining CO_2 concentration in the extracted air. A flow rate of 3 sccm, using a mass flow controller (πMFC-LP P2A, MKS), was used for complete extraction of CO_2 and simultaneous determination of CH_4 in the CO_2-extracted-air. The extraction procedure was optimized by extractions performed with a reference-air (#2) filled "dummy" sampler (≈ 50 ml), similar to the SAS. The extraction

20   efficiency was verified by comparison of the change in CO_2 signal with introduction of nitrogen (as zero-gas) and CO_2-extracted reference air into the CRDS analyzer from the dummy sampler. The process of optimization is shown in Fig. 2 b & c. Shown in Fig. 2b is a time series plot showing consecutive introduction of a zero gas (N_2, first two drops in the CO_2 and CH_4 signal; orange background) followed by CO_2 extracted reference air (#2, last two drops in the CO_2 signal; pink background). In between the consecutive measurements of N_2 (1 & 2) and CO_2 extracted reference air (3 & 4), reference air

25   (#1) was measured and is shown with a cyan background. Figure 2c shows the superimposed CO_2 signals during introduction of the zero gas (N_2) and CO_2 extracted reference air (#2) from the dummy sampler into the CRDS analyzer. This method yielded an extraction efficiency of near 100%, which was also confirmed from the pressure of CO_2 in the CO_2 trap measured during the graphitization step discussed in the next section. Although the dummy loop was filled with N_2 and reference air (#2) with very similar pressure, the superimposed CO_2 signals, in Fig. 2c, show a small difference in the total

30   running time of N_2 and CO_2 extracted reference air (#2). This is due to the fact that the reference air (#2) was cooled with liquid air during extraction, which led to a pressure drop, and thus a reduction of the total volume of air going through the CRDS analyzer before reaching the minimum differential pressure between the extraction system side and the CRDS analyzer side that the MFC could handle. As soon as the pressure in the extraction unit attained the minimum pressure (≈ 200

mbar), reference air (#1) was then directed into the CRDS analyzer and the extraction system was slowly evacuated while the CO_2 trap was still submerged in the liquid air bath. Following the complete evacuation of air from the extraction unit, the CO_2 trap was disconnected and immediately taken for graphitization, described in the next section.

The use of liquid air, during the extraction of CO_2 from air, prevented the co-freezing of CH_4 (and of oxygen). A flow rate of
5   3 sccm (standard cubic centimeters per minute) ensured ≈ 100% removal of CO_2, while allowing simultaneous determination of the CH_4 concentration. The variability in the determination of methane in CO_2 extracted air was ≤ 5 ppb. The major source of variability in the determination of the CH_4 concentration is most likely the production of CH_4 from the metal-metal friction during the operation of the stainless steel valves, both in the sampler, the extraction system and the dummy sampler (Higaki et al., 2006). During the extraction of CO_2 from the SAS, dummy extractions were also performed with reference air
10   (#2) and all extracted CO_2 samples were processed and measured by the AMS.

2.3 Graphitization

As the source of our present AMS facility is not yet capable of using gaseous CO_2, the CO_2 samples are reduced to elemental carbon, commonly referred to as graphite in the radiocarbon community. At the CIO, Groningen, the reduction of CO_2 (≈ 1-2 mg C – regular sample size) is carried out at 600 °C in the presence of H_2 (≈ 2.5 × partial pressure of CO_2) and Fe powder
15   (Alfa Aesar, 325 mesh, 2 mg) (Aerts-Bijma et al., 1997). A new graphitization system and procedure was devised later for the preparation of small samples (≈ 10-25 µgC) which featured the use of Fe in the form of a porous-pellet and not powder (de Rooij et al., 2010). For graphitization of the CO_2 samples extracted from stratospheric air, described in this work, a modified and optimized preparation method of de Rooij et al., (2010) was used. A new low-volume graphitization reactor, shown in Fig. 3, was designed in-house for the conversion of pure CO_2 into elemental carbon. The graphitization setup
20   comprised of two sections, 1) the reactor region (marked in the blue box) and 2) the mass determination region (marked in the red box). The graphitization setup was connected to a common vacuum line that also supported four other graphitization units. For evacuating the graphitization units, a turbo pumping station (Edwards, TS75W1001) was used.

The reactor region comprises of the reactor manifold, constructed from stainless steel, a reaction tube, a water trap tube and a pressure transducer. The reaction tube (od = 6 mm, id = 3 mm, length = 58 mm) and the water-trap tube (6 × 3 × 30 mm)
25   connected on the manifold were constructed from fused silica. The total volume of the reactor thus achieved was ≈ 1.5 ml. Magnesium perchlorate was used to remove water produced during the reduction of CO_2 instead of Peltier-cooled water traps, that are in use for larger samples (Santos et al., 2007a). We observed that the Peltier-cooled water traps retarded/prohibited the reduction reaction for samples below 50 µg C. Although the reduction reaction is much more efficient and faster with the use of $Mg(ClO_4)_2$, care must be taken to avoid any $Mg(ClO_4)_2$ particle entering the heated
30   section of the reactor tube, which mostly happened due to electrostatic repulsion produced through the operator. It seems likely that one of the thermal decomposition products of $Mg(ClO_4)_2$(Devlin and Herley, 1986) poisons the catalytic

properties of Fe and thus significantly slows down or even prohibits the reduction reaction. $Mg(ClO_4)_2$ in the water trap was heated to 100 °C while evacuating the system, before the graphitization step, which released a significant amount of water, making the trap even more efficient during graphitization. Iron pellets ($\approx$ 1.4 mg, 1.3 mm diameter, $\approx$ 0.4 mm thick) were prepared by pressing Fe powder (Alfa Aesar, 325 mesh) at 300 N (de Rooij et al., 2010). The reactor temperature was set at

5   500 °C, and hydrogen equivalent to $\approx$ 2.2 times the CO_2 partial pressure (at STP) was used. Hydrogen is introduced into the reactor through the vacuum line, while the CO_2 in the reactor is frozen in the water trap with liquid N_2. While introducing hydrogen in the reactor, the valve connecting the common vacuum line and the pump is closed. The reaction temperature and hydrogen pressure were optimized for minimum CH_4 production, thereby minimizing the loss of sample during the graphitization process. To optimize the reaction conditions, the production of CH_4 in the reactor was continuously monitored

10   with a residual gas analyzer (Extorr, XT100) connected to the manifold through a 25 μm (id) GC capillary column. This manifold was identical to the one used for sample preparation, except for the additional port to connect the GC capillary column (not shown in Fig. 3). The reaction time for CO_2 samples < 50 μg C was typically less than 20 min with reaction efficiency better than 95 %. The reaction progress was determined by monitoring the change of pressure inside the reactor using a pressure transducer (#1) connected on the manifold.

15   The reactor region in the setup is connected to the mass determination region, which has a known volume. This known volume was used for determining the mass of the reference gases as well as of the stratosphere CO_2 samples. As contamination is a serious concern for radiocarbon measurements of ultra small samples by AMS, it requires quantitative determination of the accumulated contaminants over the whole preparation process. Modern carbon contamination (MCC, containing contemporary levels of radiocarbon) and dead carbon contamination (DCC, originating from fossil materials with

20   no radiocarbon) affect samples differently, depending on the age and mass of the sample (Brown and Southon, 1997;Santos et al., 2007b;de Rooij et al., 2010). Very small samples such as those in the present work ($\leq$ 10 μg C) are severely affected by both MCC and DCC. Hence, for such small samples determination of the accumulated contaminating carbon is essential. To determine the mass of accumulated contaminating carbon in a sample, reference materials (with masses similar to that of the sample) containing varying levels of radiocarbon are also prepared following identical preparation steps. The extent to

25   which the reference materials deviate from the consensus value provides a direct measure of the accumulated contaminating carbon. With this information, correction of the radiocarbon values is possible (Brown and Southon, 1997;Santos et al., 2007b;de Rooij et al., 2010). This correction to the reference samples is also applied to the stratospheric samples to remove the deviations arising from contamination, assuming that all samples accumulate similar contaminations following similar preparation steps. Hence an accurate determination of the sample mass is essential.

30   Following completion of the graphitization reaction, the graphitized iron pellets were pressed on AMS aluminum holders, so-called "targets". Since these pellets are too small and the amount of material is not enough to fill the hole of the targets, a clean unused iron pellet was first dropped into the target hole on top of which the graphitized pellet was placed. This

procedure with two pellets allowed stable measurements, as the pressed target surface was much smoother this way (with only one pellet excessive fracturing of the pressed surface occurred). Each target is measured for forty minutes in the AMS and the data is analyzed offline.

The concentration of CO_2 in stratospheric air, as observed in the two collected AirCore profiles (shown in Fig. 1), was

5   between 387 and 397 ppm corresponding to 9.51-9.76 µg C in each section of the SAS. Since the mass of CO_2 from each section of the SAS was quite constant, reference samples and CO_2 samples from reference air (#2, from dummy loop) were prepared in the same mass range as the samples, a prerequisite for contamination correction. For correcting the ^{14}C in CO_2 measurements of the stratospheric air samples and CO_2 from reference air (#2), a set of three different reference materials was prepared with ^{14}C levels relevant for the present measurements. This set comprised of ANU Sucrose ($\Delta^{14}C$ = 506.1 ‰,

10   IAEA C6), HOxII ($\Delta^{14}C$ = 340.6 ‰, SRM 4990C), GS51 ($\Delta^{14}C$ Activity = 88 ‰, local reference material prepared from cane sugar acquired in November 2002). Furthermore, a background material, Rommenhöller CO_2 (virtually free of ^{14}C) was also used. All the ^{14}C activities shown in this manuscript are reported as $\Delta^{14}C$ (‰) (Mook and van der Plicht, 1999), which indicates the enrichment/depletion in $^{14}C/C$ of CO_2 with respect to the preindustrial level of 0‰. Only HOxII measurements were used to correct all the other ^{14}C activities. The two other reference materials, IAEA C6 and GS51, were used to verify

15   the effectiveness of the correction with a single reference standard, i.e. HOxII. Unlike the reference materials, which were directly graphitized from CO_2, the CO_2 samples extracted from reference air (#2) were treated following identical preparation steps, as were the CO_2 samples from stratospheric air. Figure 4 shows a summary of all the corrected ^{14}C activities of the reference materials and CO_2 from reference air (#2) relative to HOxII standards.

3. Results

20   The two AirCore samples collected on July 15th and 16th, 2014 were used to determine the radiocarbon content in the two sets of stratospheric CO_2 samples. Stratospheric air samples from the two AirCore flights were transferred into the SAS for storage, after which the SAS were brought to Groningen for further analysis. CO_2 was extracted from the samples and graphitized, pressed and measured with the AMS. The air samples stored in the SAS represented an integrated sample corresponding to an altitude range, the extent of which depended on the ambient pressure at the altitude the sample was

25   collected. The section of the AirCore profile that is transferred into the SAS can be determined based on the time it required for the sample to flow from the AirCore through the CRDS analyzer into the SAS. To verify the correctness of the altitude range derived from timing, CH_4 was used as a proxy for altitude. The decrease in the concentration of CH_4 in the stratosphere with increasing altitude is continuous and steep, making CH_4 a suitable proxy for the altitude check. In fact, CH_4 could even be used directly for altitude determination instead of the timing information. This was, however, less preferred

30   due to the production of CH_4 from stainless steel surfaces as mentioned previously, which could corrupt the CH_4 signal in an unpredictable manner and to an unknown extent. Figure 5 (a) and (b) show the results of the altitude determination from the

two stratospheric AirCore samples collected on July 15th and 16th, 2014. The blue circles show the AirCore CH_4 profile, the black solid line shows the corrected AirCore profile and the red solid line shows the predicted CH_4 concentration in each section of the SAS, based on the AirCore profile and the recorded sampling time and flow rate. Figure 5 (c) and (d) show the correlation between the CH_4 concentration as predicted based on timing, shown in (a) and (b), against concentrations

5   measured with the CRDS analyzer during extraction. For most samples, the predicted CH_4 concentration was in good agreement with the concentration measured by the CRDS analyzer during extraction. The largest deviation was observed for the sample representing the upper stratosphere (i.e. SAS section no. 6; marked with a red arrow in Fig. 5c & d) due to contaminations from leftover fill gas, which contains compressed dry ambient air (sampled at Sodankylä, Finland) spiked with carbon monoxide. This influence from the fill gas above 24 km causes the difference between the measured and the

10   corrected vertical CH_4 profiles of the atmosphere shown in Fig. 5a & b. The AirCore profiles, shown in Fig. 5, were obtained as the air from the AirCore moved through the CRDS analyzer into the sampler. During this transfer, behind the analyzer there is a small additional mixing of samples through diffusion which is not captured in the presented AirCore profile data. While diffusion in principle has slightly affected all the samples, the ones near the upper stratosphere are affected the most due to the large difference in the CH_4 concentration of the sample and the fill gas. This contamination of upper stratospheric

15   air (SAS section no. 6) with the leftover fill gas in the AirCore, due to diffusion, is predominantly the cause of the large observed deviation.

As timing is our primary parameter for altitude calculation, reliable knowledge of the timing during the filling of the SAS is crucial, i.e., the time when the valves at both ends of the SAS were closed during the filling process. "Timing" also includes here the accurate knowledge of the flow rate at which the sample from the AirCore is transferred to the SAS. A timing

20   problem was observed in the dataset shown in Fig. 5b, which could have been caused by any of the previously mentioned reasons. By introducing a "best fit" timing offset of -33 sec, we moved the whole predicted profile slightly upwards, and then the resultant predicted altitude range showed a good agreement with the measured concentrations, as seen in Fig. 5d. Control of the SAS filling process should, however, be improved, a topic for future research.

Fig. 6a shows the CO_2 concentrations retrieved from the two AirCore samples described in this manuscript (orange triangles

25   for July 15, 2014 and cyan circles for July 16, 2014) and the respective corrected AirCore profile (red line for July 15, 2014 and blue line for July 16, 2014). Figure 6b shows the measured radiocarbon concentration in the extracted CO_2 samples, with orange triangles representing samples from July 15, 2014 and cyan circles representing samples from July 16, 2014. The present $\Delta^{14}C$ value for tropospheric CO_2 is $\approx$ 20‰ (Levin et al., 2013;Graven, 2015;Hua et al., 2013). The uncertainties in the $\Delta^{14}C$ values, shown in Fig. 6b, are about ±30‰, entirely caused by counting statistics. The sample from the upper

30   stratosphere of the AirCore sampled on July 16th (sample 6) was lost during the graphitization process due to a leak in the reactor. As the production of ^{14}C from the reaction of ^{14}N with cosmogenic neutron is maximum in the stratosphere, CO_2 in the stratosphere is enriched in ^{14}C relative to the tropospheric CO_2. The transport of this enriched stratospheric CO_2 into the

troposphere (stratosphere-to-troposphere transport, STT) increases the $\Delta^{14}C$ value of the troposphere whereas the transport of tropospheric CO_2 into the lower stratosphere (troposphere-to-stratosphere transport, TST) dilutes the $\Delta^{14}C$ value of the stratosphere. This mixing in the two layers of atmosphere, very distinct in their chemical composition, through STT and TST is known as stratospheric-tropospheric exchange (STE). Caused by the nuclear bomb tests conducted during 1950's and

5   early 1960's, the atmospheric $\Delta^{14}C$ was enriched due to anthropogenic production of ^{14}C, famously known as the bomb spike. As most of the ^{14}C was produced in the stratosphere, the stratosphere-troposphere gradient was very large in those days (Nakamura et al., 1994;Nakamura et al., 1992;Ashenfelter et al., 1972). Following the Nuclear Test Ban Treaty signed in October 1963, the stratosphere-troposphere gradient gradually returned towards pre-bomb conditions, and the tropospheric $\Delta^{14}C$ has continuously dropped to a present value of $\approx 20‰$. (Zahn et al., 1999;Hesshaimer and Levin, 2000;Nakamura et al.,

10   1992;Nakamura et al., 1994).

As mentioned in the previous section, during the extraction and graphitization of the stratospheric samples, CO_2 from reference air (#2) was also extracted, graphitized and measured. AMS measurements of the 8 CO_2 samples extracted from reference air (#2, $\approx 10 \mu gC$ each), after contamination corrections yielded a mean $\Delta^{14}C$ value of 7 ± 9‰ that is in close agreement with the directly measured value of a 2 mgC sample extracted from reference air (#2) that yielded a $\Delta^{14}C$ value of

15   12 ± 4‰. This gives confidence in the applied contamination corrections.

The two CO_2 profiles shown in Fig. 6a are very similar, with slight differences near the tropopause (11-12 km, ≈ 4 ppm). The $\Delta^{14}C$ values in Fig. 6b corresponding to the lower stratosphere, sections 2, 3 and 4 of the SAS, also show very similar values for the two profiles (mean of these two times 3 values is 8 ± 8 ‰) that closely represents the current troposphere. The $\Delta^{14}C$ values corresponding to SAS section 5, in both profiles, shows some enrichment in $^{14}CO_2$ due to constant production of

20   radiocarbon in the stratosphere. In Fig. 6b, the $\Delta^{14}C$ value drops for the last sample (collected on July 15, 2014), which confirms the contamination of stratospheric CO_2 (enriched in ^{14}C) with the CO_2 from fill-gas (natural levels of ^{14}C, although the exact $\Delta^{14}C$ value is not known), as mentioned previously. The extent of contamination in the last sample from the fill gas was determined from the CO profile, since the concentration of CO in the stratosphere is low and fairly constant (≈ 15 ppb) whereas the concentration of CO in the fill gas is high and known (7972 ppb). This lead to a small correction (from 72.6‰ to

25   79.1 ± 30‰), shown with a green triangle, for contamination with $\approx 11\%$ fill gas for which we assumed a $\Delta^{14}C$ value of 20‰. The three $\Delta^{14}C$ values observed for the lower altitude samples for the July 16, 2014 profile (Fig. 5b), especially the sample close to the troposphere-stratosphere boundary (11-13 km) have ^{14}C values that are, in part significantly, lower than present day tropospheric air. The occurrence of a polluted air mass causing this can be ruled out due to the absence of a simultaneous rise of CO at such altitudes. The most probable explanation is thus contamination somewhere in the SAS

30   sampling or extraction process.

The results for these very first data sets are, due to various uncertainties (in timing and other issues such as possible sample contamination) not accurate enough to deduce any transport processes in the atmosphere; rather are these results a proof-of-

principle showing that the AirCore sampling for radiocarbon determination in stratospheric air is feasible. As the sampling method is relatively cheap, regular sample collections are affordable, leading to better understanding of the ^{14}C budget and STE transport mechanisms involved.

Conclusions

5   The results presented in this paper show that AirCore sampling is, in principle, a viable sampling method for the purpose of radiocarbon measurements in stratospheric CO_2. In this proof-of-principle experiment we achieved a measurement uncertainty of $\approx \pm$ 30‰, mostly limited by the AMS counting statistics. The $^{14}CO_2$ content in the stratosphere (up to $\approx 18 \pm 1$ km) seems very well-mixed with Δ^{14}C values being $\approx 10 \pm 8$‰, very close to the present-day troposphere. Samples from higher than 18 km, are likely to be slightly enriched in $^{14}CO_2$ ($\approx 80 \pm 20$‰), as expected in this production region of ^{14}C.

10   Since the sampling technique is relatively cheap, it is feasible to couple an AirCore "SAS" sampling program to a regular AirCore launch program, such as the one that is regularly being carried out at Sodankylä, Finland throughout the year. The stratospheric samples required for radiocarbon measurements could always be taken from any AirCore sampling and need not have to be dedicated campaigns with special protocols as long as the sample size obtained is adequate for AMS measurements. As indicated by the results in Fig. 5, one of the major challenges we faced in this work is the altitude
15   determination for each section of the SAS. In that respect, it would help if we can avoid the contamination of the CH_4 signal due to the production of CH_4 from stainless steel valves and connectors. Replacing every stainless steel valve with valves made from polymeric material might be unfeasible, but some sections can certainly be modified in the future versions. For example, currently the extraction system is completely constructed from stainless steel components, which in future can be completely replaced with glass components. This would partially reduce the extent of contamination of stratospheric air with
20   CH_4 produced because of metal-metal friction. The other important source of uncertainty in the projection of altitude is the accurate knowledge of the timing, based on which the altitude is calculated. Future experiments would require careful laboratory bookkeeping for more accurate altitude determination. Through these experiments we also learned that the samples that were collected at the top of profiles are contaminated with the fill gas, thus collecting an air column from a slightly lower altitude range would introduce less contamination. The Δ^{14}C values for the contaminated samples (last
25   sections of SAS) can also be corrected if the extent of contamination is well defined, which would require a careful characterization of the sample transfer process, from the AirCore to the SAS, or accurate measurements of CO_2 and CH_4 concentrations for these same air samples. Thus it is certainly critical to treat the stratospheric samples very carefully, and rigorous testing of the sampling process is needed to rule out leakages, potential contaminations arising from memory effects of the sampler wall and the extent of sample profile integrity as the sample from the AirCore moved into the SAS through
30   the CRDS analyzer. Additionally, the graphitization process also requires careful monitoring since incomplete reduction would result in a lower sample mass than expected in addition to isotopic fractionation, and thus a less accurate

contamination correction based on reference materials (that are then relatively larger in mass). Thus it is important to have very consistent reaction efficiencies. It is also important that the mass of the reference material, used for correction, closely matches that of the samples.

Difficulties with altitude determination and possibilities of various contamination sources notwithstanding, we successfully
5   demonstrated a new way of stratospheric ^{14}C sampling, for which we have successfully dealt with small ($\approx$ 10 µg C) samples. This is thanks to our small and efficient extraction system with near 100% extraction efficiency. With the installation of the newly designed small volume graphitization reactor, we also achieved reaction efficiencies better than 95 % for samples as small as $\approx$10 µg C. The ^{14}C ion counts can be increased further with the use of smaller Fe pellets (< 1 mg) due to the increase in the number density of the carbon atoms in the sputtered volume of the AMS target. This would
10 improve the counting statistics and thus the AMS measurement uncertainties. Alternatively, the use of a state-of-the-art AMS facility with a gas ionization source (Ruff et al., 2010;Ruff et al., 2007) would lead to less contamination (thanks to the avoidance of the graphitization step) and a higher number of accumulated counts (thanks to the higher efficiency) and thus a higher precision even with such small samples. Renewal of the current AMS system in Groningen is foreseen in the near future.

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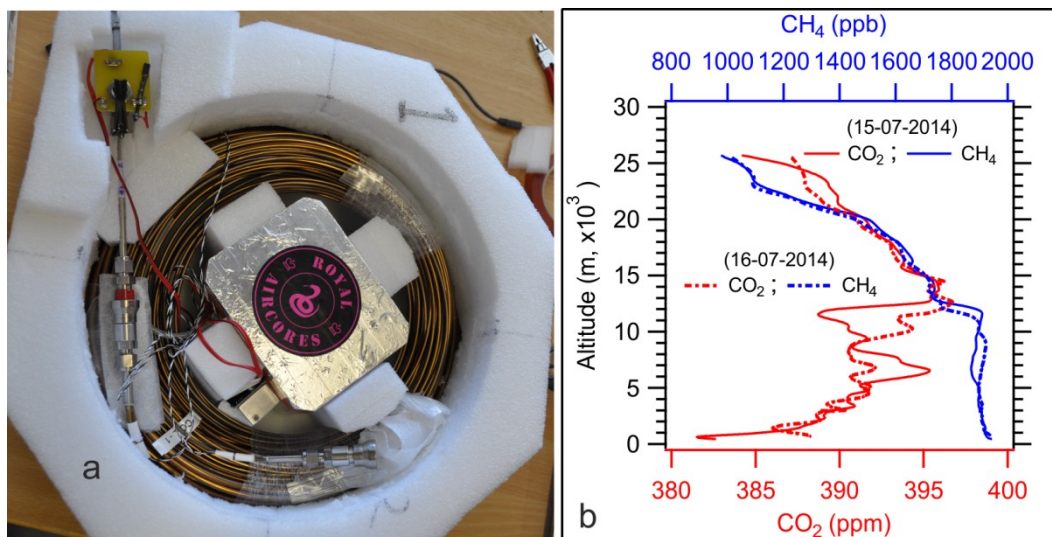
Figure 1. a) Picture of an AirCore, used during the sampling campaign at Sodankylä, constructed from a long thin walled stainless steel tubing ($\approx$ 100 m long, wall thickness = 0.254 mm). b) Corrected vertical concentration profiles of CO_2 (red) and CH_4 (blue) retrieved through AirCore samplings performed on July 15, 2014 (solid line) and July 16, 2014 (dashed line) at Sodankylä. Mind the different scale span for CO_2 and CH_4.
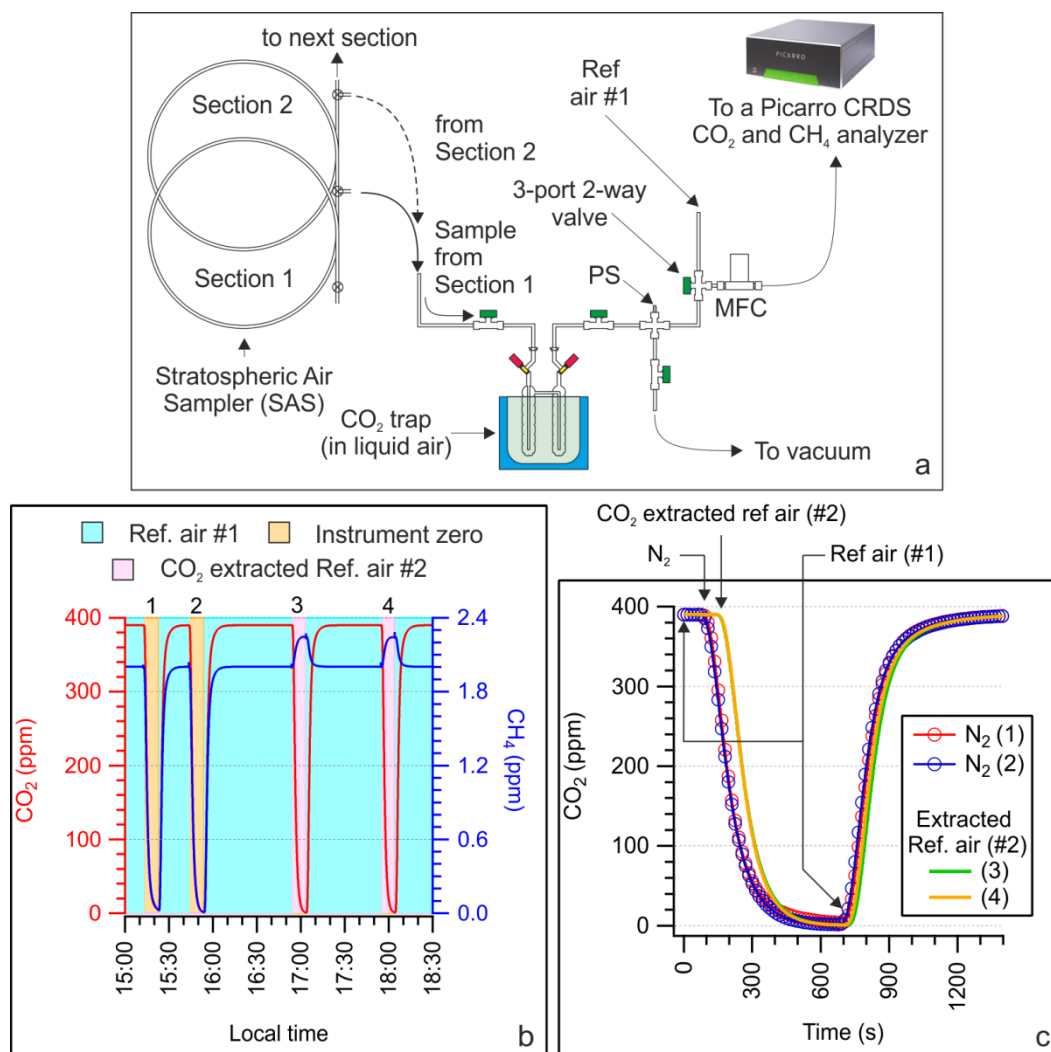
Figure 2. a) Schematic of the extraction system used for extraction of CO_2 from stratospheric air contained in the SAS. The CO_2 trap was submerged in a liquid air bath, which allowed quantitative freezing of CO_2 and avoided co-freezing of CH_4 and O_2. Using a CRDS analyzer (Picarro G2301), the concentration of CH_4 in the CO_2-extracted air was determined. The components indicated with abbreviations are as follows: MFC, mass flow controller; PS, pressure sensor. b) An example time-series showing a dummy sampler filled consecutively with N_2 (instrument zero, first two shown with an orange background) and reference air (#2, CO_2 extracted, last two shown with a pink background) to evaluate the extraction efficiency at a flow rate of 3 sccm. Reference air (#1) is directed through the Picarro analyzer when the extraction system is being made ready for the next extraction (shown with a cyan background). c) Superimposed CO_2 signal during the introduction of the zero gas (N_2) and the CO_2 extracted reference air (#2) showing a near 100% extraction efficiency.
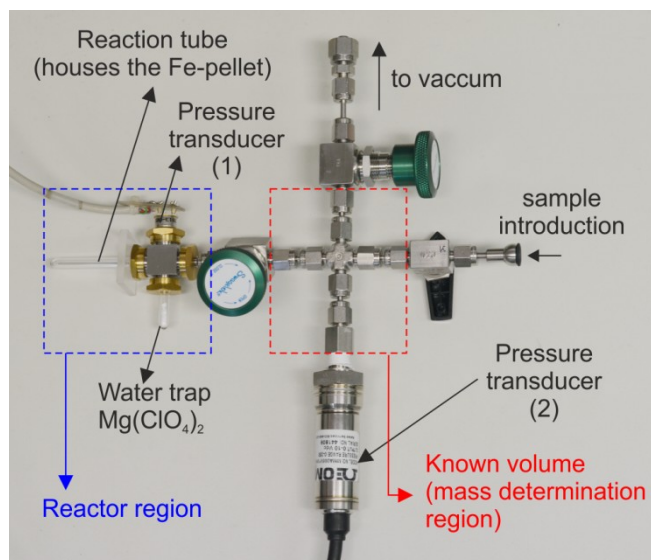
Figure 3. Newly designed reactor ($\approx$ 1.5 ml, blue box) for preparation of ultra-small samples (3-50 µgC) for AMS measurements. Each section of the stratospheric air sampler contains $\approx$ 35 µg CO_2 sample that is reduced to graphite ($\approx$ 9.6 µgC) on porous iron pellets at 500 °C in the presence of hydrogen ($\approx$ 2.2 × partial pressure of CO_2). The mass determination section, comprising of a known volume, is used to determine the mass of the reference materials and the samples based on pressure measured at pressure transducer (#2). Pressure transducer (#1) is used to monitor the progress of the graphitization reaction.
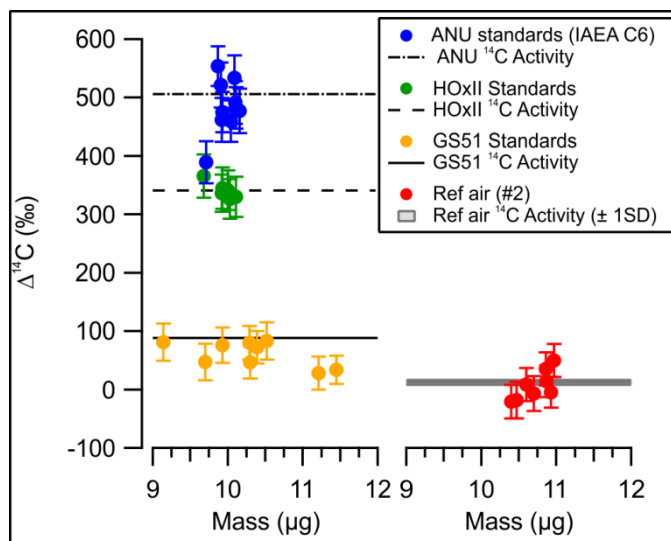
Figure 4. A summary of the derived ^{14}C activities (in Δ^{14}C, ‰) of the reference materials and CO_2 extracted from reference air (#2) relative to HOxII. All the reference samples were prepared following identical preparation steps.
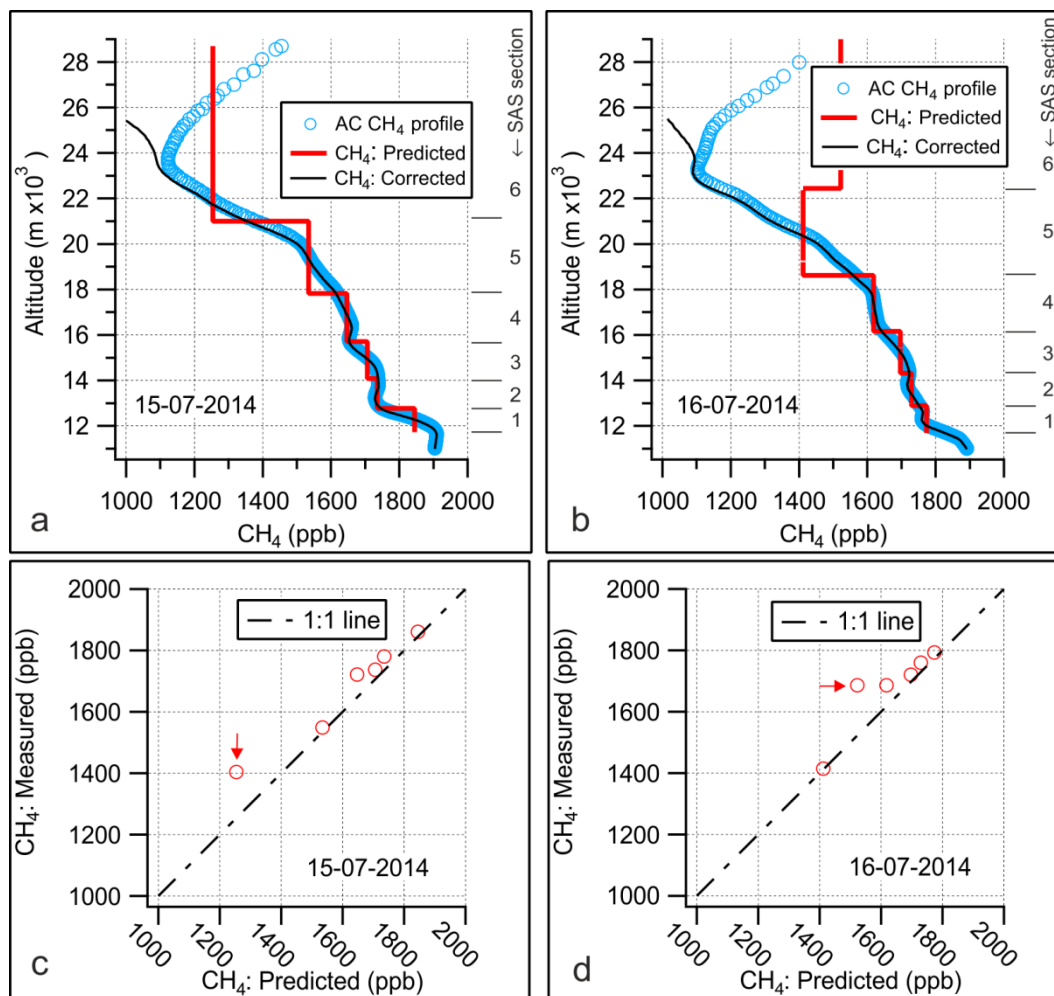
Figure 5. a) AirCore (AC) CH_4 profile (shown with blue open circles), the corrected AirCore profile (shown with a solid black line) and calculated CH_4 concentration for each section of the SAS for the samples collected on July 15, 2014. b) The same for the samples collected on July 16, 2014. c, d) Correlation between the calculated CH_4 concentration and the CH_4 concentration as measured by the CRDS analyzer while extracting the CO_2 from the samples. The measured CH_4 concentration values, for both profiles, are in good agreement with the calculated CH_4 concentrations for all samples except for the ones (indicated by arrows) corresponding to upper stratosphere, which are contaminated with leftover fill gas.
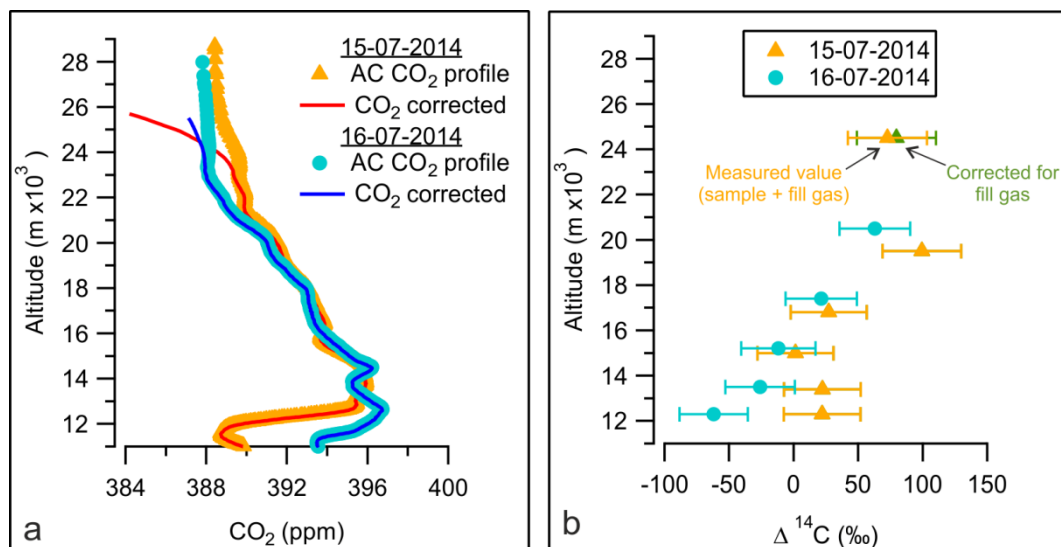
Figure 6. a) AirCore (AC) CO_2 profiles (orange triangles for July 15, 2014 and cyan circles for July 16, 2014) and their corresponding corrected AirCore CO_2 profiles (red line for July 15, 2014 and blue line for July 16, 2014). b) The $\Delta^{14}C$ values (‰, orange triangles representing samples from July 15, 2014 and cyan circles representing samples from July 16, 2014) in each section of the SAS. The $\Delta^{14}C$ value (green triangle) shown next to the sample from upper stratosphere sampled on July 15, 2014, is corrected for the fill gas contamination. The last CO_2 sample extracted from the AirCore sampled on July 16, 2014 was lost. The uncertainties in the $\Delta^{14}C$ values correspond to measurement uncertainties arising from limited counting statistics.