
Supplementary information

Preindustrial CH₄ indicates greater anthropogenic fossil CH₄ emissions

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Supplementary Information:

1. Firn and ice core air sampling methods and supporting measurements

Firn air was collected at Summit, Greenland (72.6°N 38.4°W 3214 masl) in May 2013 from a borehole drilled with the 3" US Badger Eclipse electromechanical ice drill at 20 depth levels from the surface to just above bubble close-off (80.06m) using the US Firn Air Sampling Device²⁹ following established techniques³⁰. Air samples (~100L STP) were collected at 13 of the 20 sampled depths at Summit in 35L electropolished stainless steel flasks for measurement of $^{14}\text{CH}_4$ and ^{14}CO . Aliquots from the 35L flasks were measured for $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ at INSTAAR^{31,32}, for mole fractions of CH_4 , SF_6 , CFC-11, CFC-12, CFC-113, R-134a at SIO³³ and for CO mole fraction at UR by gas chromatography with hot mercuric oxide reduction and photometric absorption. Additional samples were collected into different stainless steel flasks for measurements of $\delta^{15}\text{N}$ of atmospheric N_2 at SIO³⁴. Replicate samples were also collected into 2.5L glass flasks at 19 out of 20 depths and measured for a suite of trace gas mole fractions (CO_2 , CO, CH_4 , SF_6 , N_2O and H_2) at NOAA ESRL³⁵ and $\delta^{13}\text{C-CO}$ at INSTAAR³⁶. Mole fractions of CH_4 and CO are shown in Tables S2 and S3 and supplemental measurements are available from the NSF Arctic Data Center³⁷.

Procedural blanks were collected by introducing well-characterized standard gases into the sample inlet of the firn air system at near ambient pressure such that the gas was passed through the entire firn air sampling system at similar flowrates as during regular sampling. During this procedure the sampling system is at the surface, rather than down the borehole. Procedural blanks are analyzed alongside the regular samples. For $^{14}\text{CH}_4$, two procedural blanks were collected, one using gas from a cylinder of well characterized ambient air (with modern $^{14}\text{CH}_4$ content) and another using a synthetic mixture of air containing ^{14}C -depleted CH_4 . A pair of procedural ^{14}CO blanks were collected by flowing the modern $^{14}\text{CH}_4$ standard comprised of clean ambient air through SofnocatTM 423 reagent before sending it through the firn air system, quantitatively removing all CO (and ^{14}CO), such that any ^{14}CO present in the blanks was a result of procedural effects. Apart from CO mole fraction (Supplementary Information Section 3), the procedural blanks did not reveal any significant alterations in mole fraction or stable isotopes for any of the measured gases (Tables S2 and S3)

We further incorporate prior firn air $^{14}\text{CH}_4$ measurements from eight depth levels at the DSSW20K site at Law Dome, Antarctica⁴ in our analysis. These were collected using established techniques^{38,39} and have been analyzed for a wide range of gases and isotopes, confirming the integrity of the samples and their age distributions⁴⁰. We also include unpublished replicate analyses of $^{14}\text{CH}_4$ from firn air from a single depth at the Megadunes site in Antarctica¹⁷.

Ice core samples for $^{14}\text{CH}_4$ and ^{14}CO analyses were dry-drilled using the Blue Ice Drill⁴¹ during May-June 2015. To collect sufficiently large samples for $^{14}\text{CH}_4$ measurements, 770 – 1200 kg of ice was collected from a depth range of ~11m (Table S1). This required 2 - 3 air extractions to be performed on ice from equivalent depths in parallel boreholes and combined in the same flask to constitute a single sample. Procedural blanks were also collected for characterizing the extraneous ^{14}C added during ice core sample processing. This was done via the addition of a standard gas with a known $^{14}\text{CH}_4$ signature over meltwater remaining from a prior ice core extraction that had been purged of all dissolved CH_4 and CO, following established methods from prior studies of ice core $^{14}\text{CH}_4$ and ^{14}CO ^{8,15}. The number of blank extractions and

pressure of gas introduced to the ice melting tank were adjusted to match the number of extractions and ice core bubble volume from the sample melt extractions. Prior to ^{14}C sample processing, flasks were measured for $\delta^{13}\text{C}\text{-CO}$ and $\delta^{13}\text{C}\text{-CH}_4$ at INSTAAR^{31,36}, mole fractions of CH_4 , SF_6 , CFC-11 CFC-12 at SIO³³, and CO at UR by cavity ring down spectroscopy. Additionally, $\delta^{15}\text{N}$ of N_2 , $\delta^{18}\text{O}$ of O_2 and elemental ratios of $\delta\text{Xe/Kr}$, $\delta\text{Xe/N}_2$, $\delta\text{Kr/N}_2$, $\delta\text{Ar/N}_2$ and $\delta\text{O}_2/\text{N}_2$ were measured in the flasks at SIO following similar methods for small volume ice core samples³⁴.

2. Sample processing for ^{14}C measurement of Summit firn air samples

Firn air, ice core air samples and associated procedural blanks from Summit were processed for $^{14}\text{CH}_4$ and ^{14}CO measurements following established techniques^{8,15}. Briefly, the sample air is introduced into an ultra-clean extraction system at 1L STP/min. H_2O and CO_2 are removed cryogenically by traps cooled with a dry ice/ethanol mixture and liquid nitrogen respectively. CO in the air stream is oxidized to CO_2 at room temperature by use of SofnocatTM 423 reagent and also removed cryogenically. CH_4 is oxidized to CO_2 in an 825°C quartz furnace by passing it over 2g of a platinized quartz wool catalyst, after which the CO_2 is cryogenically purified and sealed into a PyrexTM ampoule. Resulting $^{14}\text{CH}_4$ sample sizes were $\sim 30\text{-}33\ \mu\text{gC}$ for the 2013 firn air campaign and $\sim 18\text{-}20\ \mu\text{gC}$ for 2015 ice core samples. After extraction for $^{14}\text{CH}_4$, the remaining $\sim 20\%$ of air in the flasks was diluted with a ^{14}C -depleted, high- $[\text{CO}]$ gas to increase carbon mass and bring sample ^{14}CO sample activity into the range of common ^{14}C standards¹⁵. Air processing for ^{14}CO followed the same procedure as for $^{14}\text{CH}_4$ except that the SofnocatTM catalyst was not used and the furnace was operated at 175°C to oxidize only CO into CO_2 , leaving CH_4 unaltered. Ampoules of CO and CH_4 -derived CO_2 were graphitized and analyzed for ^{14}C by AMS at ANSTO⁴²⁻⁴⁴.

Standard practice was to measure each sample for three separate 10-minute periods during the AMS analysis and to combine these as an error-weighted mean. Technical issues during the measurement run for the Summit firn air ^{14}CO and $^{14}\text{CH}_4$ samples meant that some of these samples were only reliably measured for one or two 10-minute periods. This led to higher than usual uncertainties for these measurements, however the $^{14}\text{CH}_4$ results agree with prior firn air measurements from Law Dome within uncertainties (Tables S2 and S3, Figure 1).

3. Procedural ^{14}C corrections for Summit firn air samples

The compressor pump used for pressurizing the large stainless-steel flasks produced an elevation in $[\text{CO}]$ of $3.0 \pm 2.2\ \text{nmol/mol}$ (1σ). Further, the stainless-steel flasks were re-measured for $[\text{CO}]$ prior to ^{14}C extraction and showed an increase of $20.4 \pm 10.7\ \text{ppb}$ across all flasks in comparison to 2.5L glass flasks from the same depth (Table S3). This $[\text{CO}]$ growth is well represented by the two procedural blanks collected. The sample ^{14}C content in units of ^{14}C molecules per standard cubic centimeter of air (molecules/ccSTP) is calculated for samples and procedural blanks using Equation 1:

$$[^{14}\text{C}_X] = \frac{\text{pMC}_X}{100} \times e^{-\lambda(y-1950)} \times \frac{\left(1 + \frac{\delta^{13}\text{C}_X}{1000}\right)^2}{0.9752} \times \left(\frac{^{14}\text{C}}{^{12}\text{C} + ^{13}\text{C}}\right)_{\text{abs}} \times [X] \times \frac{1}{22414} \times N_A \quad (1)$$

In this equation, X represents the gas of interest (CO or CH_4), $[X]$ represents the mole fraction of gas X, pMC_X denotes the measured ^{14}C activity of gas X after procedural corrections in units of percent modern carbon⁴⁵, λ is the ^{14}C decay constant ($1.210 \times 10^{-4}\ \text{yr}^{-1}$), y is the year

of AMS measurement, $\delta^{13}\text{C}_x$ is the measured $\delta^{13}\text{C}$ of the gas, 0.975 is a factor arising from ^{14}C activity normalization to $\delta^{13}\text{C}$ of -25‰ within the definition of pMC, $^{14}\text{C}/(^{12}\text{C}+^{13}\text{C})_{\text{abs}}$ reflects the abundance of ^{14}C relative to the stable isotopes in the absolute ^{14}C standard⁴⁶ (1.176×10^{-12}), 22414 represents the number of cubic centimeters of gas at STP (ccSTP) per mole, and N_A is the Avogadro constant.

We subtracted the ^{14}CO content of the procedural blanks from each firn air sample in units of molecules/ccSTP to arrive at the true corrected ^{14}CO content in the firn air. Interaction between thermal neutrons generated in the atmosphere and N_2 in air tanks has been shown to constitute a significant source of ^{14}CO and is likely the main source of extraneous ^{14}CO in the firn air samples⁴⁷. This is especially significant at a high altitude, high latitude location like Summit, as the tanks were kept on site for 5-17 days after they were collected. The two procedural blank samples were collected 11 days apart, with the firn air samples collected in the days between. Thus, to approximate the time-dependent effect of in situ ^{14}CO production in the sample tanks, we interpolated the procedural ^{14}CO content in our samples based on the date they were collected in relation to the dates that the procedural blanks were collected.

Procedural $^{14}\text{CH}_4$ corrections for extraneous C addition are applied similar to prior studies of ice core $^{14}\text{CH}_4$ ^{8,15} and use a Monte Carlo routine for error propagation. Stepwise corrections for $^{14}\text{CH}_4$ content are shown in Table S2.

4. Sample processing and procedural corrections for Megadunes and Law Dome firn air samples:

Firn air in the Law Dome DSSW20K and Megadunes samples was processed (for $^{14}\text{CH}_4$ only) using a separate system at the National Institute of Water and Atmospheric Research (NIWA)^{48,49}. The efficiency of CO removal prior to CH_4 oxidation was estimated at better than 99 % by GC measurements⁴⁸ and during this measurement period by tests involving ^{13}C -labelled CO. 0.45 ± 0.45 pMC was subtracted from the graphitization blank-corrected ^{14}C values in these samples to account for potential breakthrough of ^{14}CO in the extraction line. Additionally, measurements of CFCs in the Megadunes samples indicate that the samples contained ~0.5% admixed younger air from above (mean age ~1997). We use an isotope mass balance expression with an assumed $^{14}\text{CH}_4$ activity of 130 pMC on the admixed air to arrive at an additional correction of 0.33 ± 0.17 pMC that was subtracted from the measured ^{14}C values for the two Megadunes samples. Stepwise corrections for $^{14}\text{CH}_4$ content are shown in Table S2.

5. Correction for in situ cosmogenic $^{14}\text{CH}_4$ in firn air samples

Energetic neutrons⁵⁰ and muons⁵¹ produce ^{14}C directly within the ice crystal lattice via interactions with ^{16}O . This ^{14}C is quickly oxidized to ^{14}CO or $^{14}\text{CO}_2$, yet a small amount of $^{14}\text{CH}_4$ is also formed^{15,52}. The majority of in situ cosmogenic ^{14}C appears to be quickly lost from the ice grains into the firn air open porosity and subsequently into the overlying atmosphere^{52,53}. As a result, in situ cosmogenic ^{14}C largely accumulates in and below the lock-in zone (LIZ), where firn transitions to ice (below ~68m depth at Summit). At such depths, the mechanism for ^{14}C production is by muons and the ratio of $^{14}\text{CH}_4/^{14}\text{CO}$ produced (0.00759 ± 0.00030) has been shown to be constant¹⁵. This enables an empirical correction for in situ cosmogenic $^{14}\text{CH}_4$ using estimated in situ cosmogenic ^{14}CO content. Figure S1A shows measured firn air [^{14}CO], illustrating the rapid accumulation of in situ ^{14}CO in the LIZ. Atmospheric (not in situ) ^{14}CO is a large part of the overall ^{14}CO signal in the Summit samples, thus the atmospheric ^{14}CO history needs to be accounted for when quantifying the in situ ^{14}CO component.

The primary component of atmospheric ^{14}CO (~90% for air at Greenland Summit) is produced in the upper atmosphere by cosmic ray neutrons^{54,55}. Mean annual ^{14}CO concentration is largely controlled by the ^{14}C production rate which varies with the 11 year solar cycle, as shown by measurements in the Southern Hemisphere⁵⁶ (Figure S2A). There have been no prior measurements of atmospheric ^{14}CO at Summit and only short (1 – 3 yr) records from the mid-late 1990's at high northern latitude sea level sites⁵⁴. For estimating the paleoatmospheric [^{14}CO] in our ice core and firn air samples, we use the longest available record of atmospheric ^{14}CO measurements covering a full solar cycle⁵⁶ and apply a 12-month moving average after subtracting the secondary component (~10%) that arises from CH_4 , Non- CH_4 hydrocarbon oxidation, and biomass burning⁵⁴. The relationship between sunspot group number⁵⁷ and the primary mean annual ^{14}CO is then determined via a linear regression. Southern Hemisphere ^{14}CO is known to be lower than Northern Hemisphere ^{14}CO at equivalent latitudes⁵⁴. We apply a constant offset (10.23 molecules/ccSTP) to the mean annual Southern Hemisphere ^{14}CO record to match the reconstruction with what is observed in the Summit firn air samples that are not significantly affected by the ^{14}CO seasonal cycle or in situ cosmogenic production (Figure S2A). This offset accounts for both the higher mean annual ^{14}CO at Summit as compared to the Southern Hemisphere and the secondary component of ^{14}CO (this component was removed from the Southern Hemisphere data for the analysis in Fig 2A). Finally, historical mean-annual atmospheric ^{14}CO is calculated for the length of the sunspot group number record using the relationship observed during solar cycles 22-23 (1989-2002) (Figure S2B). We note that while the changes between solar cycles impose some uncertainty in our reconstruction of paleoatmospheric ^{14}CO , the age distributions of our ice core samples do not include significant quantities of air from the Maunder and Dalton sunspot minima⁵⁷ where this relationship is least likely to be maintained (Figure S2B). Overall, we use a $\pm 12.5\%$ (1σ) uncertainty on the reconstructed history to account for the uncertainties involved in relating northern hemisphere atmospheric ^{14}CO to solar variations.

For the Summit firn air samples, we implemented the calculation of in situ cosmogenic ^{14}C within the forward firn air model (Supplementary Information Section 7) using ^{14}C production rates derived from ablating ice¹⁵ and scaling factors⁵⁸ to account for the changes in altitude and geomagnetic cosmic ray shielding at different ice coring sites. Combined with the atmospheric history of ^{14}CO developed from sunspot group number, the model calculates the expected total firn air ^{14}CO content (paleoatmospheric + in situ cosmogenic). The in situ cosmogenic ^{14}CO production and retention through the firn column calculated by the model is tuned to match the observed ^{14}CO measurements at Summit (Figure S1A, red trace). Once tuned, the model is run with the atmospheric history of ^{14}CO set to 0, thus calculating only the in situ cosmogenic component of ^{14}CO in the firn air samples (Figure S1A, yellow trace; Table S3). In situ cosmogenic $^{14}\text{CH}_4$ is then calculated using the constant $^{14}\text{CH}_4/^{14}\text{CO}$ ratio from production by muons¹⁵ and Equation 1 is applied to convert the in situ $^{14}\text{CH}_4$ into pMC units (Table S2).

We do not have measurements of ^{14}CO at Megadunes for comparison with the firn model, and the available measurements of ^{14}CO at Law Dome DSSW20K show unrealistically high variability⁵⁹. Here we estimated the cosmogenic component of ^{14}CO by using the same ^{14}C production and retention rates as for Summit, only accounting for the effects of latitude and altitude on the cosmic ray flux⁵⁸. Due to the uncertainties involved in translating the ^{14}C production rates between different sites, we apply a large uncertainty (100% in the shallow firn, 50% in the lock in zone) to the calculated in situ $^{14}\text{CH}_4$ component (amounting to 1.11 pMC at

Megadunes and 0.36 pMC at the deepest Law Dome sampling depth). Overall, the in situ cosmogenic $^{14}\text{CH}_4$ correction at all firn air sites amounts to <1.1% of total $^{14}\text{CH}_4$ and is on par with or smaller than the analytical precision of the AMS measurement.

6. Procedural ^{14}C corrections for Summit ice core $^{14}\text{CH}_4$ and ^{14}CO

Procedural corrections and the approach for calculating ice core $^{14}\text{CH}_4$ and ^{14}CO content have been described in detail in previous studies^{8,15}; Here we only describe calculations that differ from the prior work. As in the firn air samples, in situ cosmogenic ^{14}CO in the ice core samples is used to constrain the in situ cosmogenic $^{14}\text{CH}_4$ content. Paleoatmospheric ^{14}CO content and procedurally-added [CO] (and its ^{14}C signature) must be quantified and subtracted to determine the in situ cosmogenic ^{14}CO component (Table S7). Paleoatmospheric [^{14}CO] in each sample is calculated by convolving the [^{14}CO] history developed for Summit with the sample CO age distributions from the firn forward model (Supplementary Information Section 7, Figure S2B).

The largest source of procedurally-added ^{14}CO for the ice core samples is in situ ^{14}CO production in the sample canisters, same as for firn air samples (Table S7). This ^{14}CO contribution is corrected for via subtraction of the mean ^{14}CO measured in the two procedural blanks. Estimating the component of procedurally-added ^{14}CO that is not captured by the procedural blanks requires an estimate procedurally-added [CO] that is similarly not captured by the procedural blanks (Table S5). This in turn requires comparing [CO] measured in our samples (after procedural blank [CO] subtraction) with the paleoatmospheric [CO] trapped in the ice. For this purpose, we developed a mean annual High Latitude Northern Hemisphere [CO] history for Summit (Figure S1B) from a compilation of several records over different age ranges: 1600-1900 from a spline fit to the Eurocore ice core measurements^{60,61}, 1950-2004 from a reconstruction based on firn air measurements at NEEM, Summit and NGRIP⁶² and 2000-present from direct flask measurements at Summit as part of the NOAA CCG monitoring network⁶³. The most uncertain part of the record is from 1900-1950, since the most recent datum from Eurocore (~109 nmol/mol in 1947)⁶¹ does not agree with the range of 140-150 nmol/mol in 1950 from the compilation of firn air records⁶². Due to this disagreement between records, and higher confidence in the more recent multi-site firn air compilation, we use the entirety of the 1950-2000 firn air record and allow for a cubic smoothing spline to approximate the [CO] in 1900-1950 so that the gradual increase beginning ~1880 is accelerated to be compatible with the firn air record. The uncertainty (1σ) we apply to the reconstruction (grey shading in Figure S1B) is ± 3 nmol/mol for the NOAA flask measurements, ± 5 nmol/mol for the multi-site firn air reconstruction 1950-2004, ± 25 nmol/mol for the most uncertain interval from 1900-1950 and ± 10 nmol/mol before 1900. The trapped paleoatmospheric [CO] in the ice core samples is estimated by convolution of the mean annual [CO] reconstruction described above and the age distribution for CO in each ice core sample (Figure S2B).

Procedurally-added [CO] that is not accounted for by the full-process procedural blanks is estimated to be ~110 nmol/mol for the three ice core samples (Table S5). Lacking a precise constraint on the origin of this CO and its ^{14}C activity, we assume an activity spanning the full range of 0-100 pMC in a uniform probability distribution and calculate the [^{14}CO] generated by procedural effects to be subtracted from each sample using Equation 1. Values from stepwise corrections applied for [CO] and [^{14}CO] can be found in Tables S5 and S7.

Procedural corrections for $[\text{CH}_4]$ and $^{14}\text{CH}_4$ also follow prior studies^{8,15} and values involved in the corrections are shown in Tables S4 and S6. After these corrections, we calculate the sample $^{14}\text{CH}_4$ content in molecules/ccSTP using Equation 1. Similar to the firn air samples, the estimated in situ cosmogenic ^{14}CO content in the samples and the in situ cosmogenic $^{14}\text{CH}_4/^{14}\text{CO}$ ratio¹⁵ is used to calculate the in situ cosmogenic $^{14}\text{CH}_4$ content in the samples, and this is subtracted from the total $^{14}\text{CH}_4$ content. The corrected $^{14}\text{CH}_4$ value is then converted back into pMC units and then into age-corrected $\Delta^{14}\text{CH}_4$ units by Equation 2, where x is the mean age of the sample air (Figure S3B). Overall, the in situ cosmogenic $^{14}\text{CH}_4$ component comprises 0.9-1.9% of the total $^{14}\text{CH}_4$ signal in each of the ice core samples.

$$\frac{\text{pMC}}{100} = \left(\frac{\Delta^{14}\text{CH}_4}{1000} + 1 \right) e^{\frac{(x-1950)}{8267}} \quad (2)$$

7. Forward firn air model

The gas age distributions of the firn air and ice core samples (Figure S3) are simulated using a firn gas transport model¹⁸. The forward model is used to simulate the age distributions of CH_4 with depth at each sampling site in both open and closed pores; the latter are calculated using a stochastic layered bubble trapping process⁶⁴. We follow the same method as described in ref. ¹⁸ for tuning the diffusivity profile at each of the sites (Summit, Law Dome DSSW20K and Megadunes) and constraining the model uncertainty, with a few modifications as follows. (1) $^{14}\text{CO}_2$ was not used as a tracer gas due to uncertainty about the magnitude of in situ cosmogenic $^{14}\text{CO}_2$ production. (2) $\delta^{15}\text{N}_2$ was also not used due to observed thermal fractionation signal from recent warming⁶⁵ and seasonal temperature gradients⁶⁶ that are not well-captured by the steady state model. (3) N_2O was included as a tracer gas using a recently developed multi-site reconstruction from firn air⁶⁷. (4) All tracer gas atmospheric histories are updated through December 2015 with monthly mean flask measurements from Summit Station by NOAA ESRL^{63,68} and converted to the most recent NOAA measurement scales⁶⁹. (5) Radioactive decay of ^{14}C is not considered within the forward firn model and considered elsewhere due to concerns with the ^{14}C age correction for multiple sites as described in Supplementary Information Section 9.

8. Depth scale and ice thinning corrections for ice core samples

The ice layer age at depth is simulated in the firn air model by integrating the firn density (based on a spline fit to high-resolution measurements⁷⁰) from the surface to depth, and dividing this by the accumulation rate and by the pure ice density⁷¹. The accumulation rate is then tuned to data acquired via continuous flow analysis (CFA) measurements. For the 2013 firn air borehole we have three volcanic markers (Tambora, Laki and an unknown eruption in 1810) in the lock-in zone (occurring at 67.6, 76.5 and 69.2m respectively) to use as constraints for an ice age scale. For the 2015 core we used multi-parameter annual layer counting from CFA measurements in 80-98 m depth range⁷² on ice collected from a parallel borehole. The distinct annual minimum in the non-sea-salt sulfur to sea-salt sodium ratio was assigned to January 1 each year and confirmed using fallout from well-dated volcanic events⁷³. To quantify the magnitude of ice thinning present at Summit, we make use of a Dansgaard-Johnsen (DJ) type thinning model⁷⁴ run in ice-equivalent depth and then converted back into true depth.

Accounting for the thinning of ice, we find a best fit between the available chemistry measurements and predicted ice age from the firn air model (including the thinning correction)

with an accumulation rate of 0.246 m/yr ice equivalent. Incorporating the effects of ice thinning (~5% at 130m depth) within the already established forward firn model would lead to a non-steady state condition and significantly more difficult model parameterization. Instead we incorporate the effects of ice thinning by running the forward firn model at an artificially lower accumulation rate (0.235 m/yr) such that the ice age scale calculated by the firn air model matches the age scale from the available chemistry measurements between 68-98m depth. This approach leads to a slight over-estimation of the depth in the deepest sample (125-135m) as compared to the approach that incorporates an explicit thinning function. This is corrected for by a shift of the actual sampling depths to depths predicted by the firn model with the reduced accumulation rate (Table S1). Since the firn model behavior is tuned to measurements made in 2013, we also account for the two extra years of accumulation for the 2015 ice samples so that their depths correspond to where the firn models predict those ice parcels would have been in 2013.

9. Inverse firn air model

To invert the firn air and ice core $^{14}\text{CH}_4$ measurements into an atmospheric history, we use the forward firn air model to develop distributions of gas age vs depth (transfer functions) at each firn air and ice core site¹⁹. Transfer functions are generated separately for each isotopologue of interest ($^{12}\text{CH}_4$ and $^{14}\text{CH}_4$) by defining the atomic mass and diffusion coefficient for each isotopologue rather than by the mean value for all isotopologues (Table 5 and Equation 6 in the supplementary information to ref¹⁸). The transfer functions are then converted into a kernel (G, from ref¹⁹) that represents the gas age distribution for each of the $^{14}\text{CH}_4$ measurements (firn or ice). The gas age distribution for the ice core samples (as used in the Kernel G) is averaged over the entire ~11m depth range where the samples were taken from (Figure S3B and Table S1). Our kernel combines firn (open pores) and ice (closed pores) samples, as well as samples from different sites; each measurement is included with its specific age distribution in calendar years. This way, a single atmospheric reconstruction is found in the inversion that is constrained by all available measurements simultaneously⁷⁵. In matrix notation, the forward problem is defined as¹⁹:

$$\mathbf{G}\mathbf{h} = \mathbf{m} \quad (3)$$

With $\mathbf{h}$ representing the atmospheric history of the trace gas mole fraction under consideration, G the Kernel, and $\mathbf{m}$ the modeled trace gas mole fraction for each of the available measurements. We apply three different inverse methods of reconstructing the atmospheric $^{14}\text{CH}_4$ history from the firn and ice measurements. The inversion is done in $\delta^{14}\text{C}$ units, and age-corrected outside of the inverse model (details below). The first method is the matrix inversion of ref.¹⁹ slightly modified to allow it to be used for isotope ratios. The estimated atmospheric history $\mathbf{h}_{\text{est}}$ is then found from the observations $\mathbf{m}_{\text{obs}}$ via matrix inversion using Equation 35 from ref.¹⁹:

$$\mathbf{h}_{\text{est}} = (\mathbf{G}^T \mathbf{W}_e \mathbf{G} + \kappa^2 \mathbf{W}_m)^{-1} \mathbf{G}^T \mathbf{W}_e \mathbf{m}_{\text{obs}} = \hat{\mathbf{G}} \mathbf{m}_{\text{obs}} \quad (4)$$

In this equation, $\mathbf{W}_e$ represents a diagonal weighting matrix with the inverse of the data variance (σ^{-2}), $\mathbf{W}_m$ the square of a tridiagonal matrix with 1 in its main diagonal and -1/2 in the upper and lower off-diagonal, and κ a regularization parameter that controls the smoothness of the solution¹⁹. Since isotope ratios are not mass conserving, we need to invert the major (^{12}C) and minor (^{14}C) isotopologues separately:

$$\mathbf{h}_{\text{est}}^{12} = \widehat{\mathbf{G}}^{12} \mathbf{G}^{12} \mathbf{h}_{\text{CH}_4} \quad (5)$$

$$\mathbf{h}_{\text{est}}^{14} = \widehat{\mathbf{G}}^{14} \left(\mathbf{G}^{12} \mathbf{h}_{\text{CH}_4} \circ \left(\frac{\mathbf{m}_{\text{obs}}^{\delta}}{1000} + 1 \right) \right) \quad (6)$$

In the above equations, $\mathbf{h}_{\text{CH}_4}$ represents the reconstructed atmospheric CH_4 mixing ratio, $\mathbf{m}_{\text{obs}}^{\delta}$ the observations in isotopic delta notation and $\circ$ the Hadamard (or entry-wise) vector product. Note that $\mathbf{G}$ is isotope-specific since each has a different mass and diffusion coefficient, thus the absolute isotopic abundances are irrelevant given that the forward model is linear. The estimated atmospheric history of $^{14}\text{CH}_4$ expressed as an isotopic ratio $\delta^{14}\text{CH}_{4,\text{atm}}$ is then given by:

$$\delta^{14}\text{CH}_{4,\text{atm}} = \left(\frac{\mathbf{h}_{\text{est}}^{14}}{\mathbf{h}_{\text{est}}^{12}} - 1 \right) \cdot 1000\text{‰} \quad (7)$$

The other two inversion methods both rely on the fact that the forward problem (Equation 3) is numerically cheap to solve. In these methods, $\delta^{14}\text{CH}_{4,\text{atm}}$ is approximated using a cubic smoothing spline to a series of coefficients $[\mathbf{h}_i]$, giving the isotopic ratio at each model timestep, i . We use the MATLAB function “csaps” for the cubic smoothing spline, again with a regularization parameter κ to control smoothness of the solution. The goodness-of-fit for any given set of coefficients $[\mathbf{h}_i]$ is evaluated by solving the forward problem for each isotopologue:

$$\mathbf{m}^{12} = \mathbf{G}^{12} \mathbf{h}_{\text{CH}_4} \quad (8)$$

$$\mathbf{m}^{14} = \mathbf{G}^{14} \mathbf{h}_{\text{CH}_4} \circ \left(\frac{\delta^{14}\text{CH}_{4,\text{atm}}}{1000} + 1 \right) \quad (9)$$

after which the goodness-of-fit can be evaluated via the model-data offset:

$$\mathbf{m}_{\text{obs}}^{\delta} - \left(\frac{\mathbf{m}^{14}}{\mathbf{m}^{12}} - 1 \right) \cdot 1000\text{‰} \quad (10)$$

We optimize $[\mathbf{h}_i]$ either using a gradient method, or via a Monte-Carlo approach with a Metropolis sampling algorithm⁷⁶.

The radioactive decay of ^{14}C (5730 ± 40 year half-life⁷⁷) requires extra care with the analyses to ensure that it is considered only once within our calculations. The ^{14}C data are loaded into the inverse model in the age-corrected $\delta^{14}\text{C}$ unit (δ), that removes normalization to the sample ^{13}C and accounts for ^{14}C decay since formation⁷⁸.

$$\left(\frac{\delta}{1000} + 1 \right) = \frac{A_S e^{\lambda(1950-x)}}{A_{ON}} \quad (11)$$

This is chosen so that data from multiple ice core sites, all collected and analyzed in different years, can be considered within with normalization to the same ^{14}C standard that is set to the year 1950. Additionally, since the inversion is performed comparing only the $^{12}\text{CH}_4$ and $^{14}\text{CH}_4$ isotopologues, we remove the ^{13}C normalization from the samples before the inversion, then after the inversion apply a ^{13}C correction based mean annual atmospheric $\delta^{13}\text{CH}_4$ interpolated from ice core and firn air records^{79,80}, which puts our reconstruction defined in equation 11 into a more familiar age-corrected $\Delta^{14}\text{C}$ notation defined in Equation 2, $\Delta^{14}\text{CH}_{4,\text{atm}}$.

Since the atmospheric inversions used here consider the atmospheric history of the trace gas, the different masses and diffusion coefficients of the isotopologues; the effects of gravitational⁸¹ and diffusive fractionation⁸² are accounted for in our method. We combined sites

from the Northern and Southern hemispheres, assuming that the interhemispheric $\Delta^{14}\text{CH}_4$ gradient is much smaller than the signal we try to reconstruct.

To estimate the uncertainty in $\Delta^{14}\text{CH}_{4,\text{atm}}$ we run the inversion 10,000 times for each of the three methods, where each time we apply random perturbations to $\mathbf{m}_{\text{obs}}^\delta$, the width of the gas age distributions in the kernel, and the smoothness parameter κ to get a realistic sense of how the solution depends on these uncertain parameters. Solutions from the three different approaches are compared in Figure S4 and show good agreement (within uncertainty) from 1850 onward, where we have good data constraints.

10. Box model calculation of fossil CH_4 source history

We first determine the global atmospheric CH_4 burden (M_{CH_4}) from the global CH_4 mole fraction reconstruction¹ using a conversion factor of 2.787 Tg CH_4/ppb ⁸³. We then use a 1-box model calculation to estimate the total CH_4 source to the atmosphere (Q_{total}):

$$\frac{dM_{\text{CH}_4}}{dt} = Q_{\text{Total}} - \frac{M_{\text{CH}_4}}{\tau} \quad (12)$$

For the CH_4 lifetime (τ), we use 9.1 ± 0.9 (1σ) years in 2010 and 9.5 ± 1.3 years in 1750⁸³ and linearly interpolate for ages in between. Next, we calculate the fossil fraction of the atmospheric methane burden (FF_{M,CH_4}) based on the comparison of our $^{14}\text{CH}_4$ history developed from the inverse model ($^{14}\text{CH}_{4,\text{atm}}$) in pMC units.

$$FF_{M,\text{CH}_4} = 1 - \frac{^{14}\text{CH}_{4,\text{atm}}}{^{14}\text{CH}_{4,\text{Bio source}}} \quad (13)$$

Since our inversion uses data from both hemispheres, we use the average of IntCal13⁸⁴ and SHCal13⁸⁵ as representative of the global atmospheric $^{14}\text{CO}_2$ history prior to 1950. We then apply a 6-year mean exponential distribution to the $^{14}\text{CO}_2$ history to account for the delay between uptake of atmospheric CO_2 and emission as CH_4 from biogenic sources and biomass burning⁴ to arrive at the biogenic source signature ($\Delta^{14}\text{CH}_{4,\text{Bio source}}$, blue trace in Figure 1). We use the global mean atmospheric $^{14}\text{CO}_2$ record⁸⁶ to calculate the biogenic source signature for the post-bomb era shown in Figure 1 (1950-present); however, this time period is not considered in our box model calculation due to large uncertainties in nuclear $^{14}\text{CH}_4$. Additionally, the fossil fraction can be expressed as the ratio of fossil to total CH_4 sources, $Q_{\text{Fos}}/Q_{\text{Tot}}$. By including the fossil fraction (Equation 13) in the box model (Equation 12), Q_{Total} then transforms into the fossil source (Q_{fos}), which can be solved for at all timesteps for which we have a $^{14}\text{CH}_4$ history to calculate the fossil fraction.

$$Q_{\text{Fos}} = \frac{d(M_{\text{CH}_4} \cdot FF_{M,\text{CH}_4})}{dt} + \frac{M_{\text{CH}_4} \cdot FF_{M,\text{CH}_4}}{\tau} \quad (14)$$

We implemented a Monte Carlo algorithm for the calculations above with a 1year timestep, perturbing each input parameter within its respective uncertainties and repeating the calculation 30,000 times. For the $^{14}\text{CH}_4$ history, we use all 30,000 independent reconstructions calculated from the inverse firm model for each of the three methods described in Supplementary Information Section 9. For the remaining parameters ($^{14}\text{CH}_{4,\text{Bio source}}$, M_{CH_4} and τ) we perturb the value at each box model timestep with a 1σ normally distributed random error, as well as a constant 1σ normally distributed random error at all time steps based on the reported uncertainty of τ ⁸³, the reported uncertainty of the $^{14}\text{CO}_2$ record for $^{14}\text{C}_{\text{Bio source}}$ ^{84,85}, and an assumed $\pm 1\%$ (1σ)

uncertainty for M_{CH_4} . For each MC iteration, we apply a gaussian-weighted moving average filter over a 25 year window on the timeseries of $^{14}C_{Bio, source}$, M_{CH_4} and τ to eliminate the unphysical noise generated by perturbing the parameters at each timestep. We note that this applies a similar level of smoothing to what is seen in ice core and firn air samples due to gas diffusion in the firn.

Due to the gap in our ice core age distributions between ~1800-1850, we cannot develop a continuous reconstruction of $^{14}CH_4$ before 1850. For the deepest ice sample not covered by the continuous reconstruction (mean age 1756), we calculate a fossil fraction (Equation 13) in each year covered by that sample's air age distribution (Figure S3B, red trace) by comparing the measured $^{14}CH_4$ activity of that sample with the contemporaneous source $^{14}CH_4$ history. Under the assumption that the atmosphere is in steady state with respect to natural fossil CH_4 emissions over the time interval covered by the age distribution (1700 – 1800), we get:

$$Q_{Fos} = \frac{M_{CH_4} \cdot FF_{M,CH_4}}{\tau} \quad (15)$$

Using the M_{CH_4} and τ developed for the timeseries above, we calculate a “steady-state” Q_{Fos} at each year and weight the results according to the air age distribution of that sample. We implement normally distributed random error in each parameter and repeat the calculation 100,000 times, neglecting negative fossil fraction values (which are unphysical) and resample only the positive values. This results in a median value of 1.6 Tg CH_4 /yr for natural fossil $^{14}CH_4$ emissions ($Q_{Fos,Nat}$) with a 95% CI maximum of 5.4 Tg CH_4 /year (Figure S5).

We conducted a sensitivity analysis to assess the impact of uncertainties involved in our estimate of preindustrial era fossil CH_4 emissions. This was assessed for each key input parameter in the box model (M_{CH_4} , τ , $^{14}CH_{4,bio\ source}$) and major source of uncertainty in calculating the preindustrial era $\Delta^{14}CH_4$ value (AMS ^{14}C measurement precision, in situ cosmogenic and procedural ^{14}C corrections). The analysis was performed by repeating the Monte Carlo calculation described above with one input parameter fixed at the upper or lower 95% CI limits based on the uncertainties described above and the remaining parameters unchanged from their reported values and uncertainties. The resulting median and 95% CI for $Q_{Fos,Nat}$ for each case are reported in Table S8. The uncertainty in the measured ^{14}C value for the deepest ice core sample (resulting from analytical precision on the AMS) has the largest effect on the median estimate of natural fossil CH_4 emissions ($\pm_{-1.4}^{+2.0}$ Tg CH_4 /yr). We note that while the correction for in situ cosmogenic ^{14}C introduces the largest change in the $^{14}CH_4$ value (-1.70 pMC, Table S6), yet its uncertainty (± 0.13 pMC, 1σ) is smaller than the precision of the AMS ^{14}C measurement (± 0.78 pMC, 1σ) and the uncertainty in the procedural correction (± 0.63 pMC, 1σ). The impact of the uncertainty in the in situ cosmogenic correction on the estimated preindustrial era fossil CH_4 emissions is thus very small (Table S8).

11. Box model calculation of modern fossil CH_4 source using $\delta^{13}CH_4$

To assess the implications of our $^{14}CH_4$ constraints on the modern fossil CH_4 budget, we repeat the $\delta^{13}CH_4$ -based 1-box model calculation of a recent study³ using our probability distribution of natural fossil CH_4 emissions ($Q_{Fos,Nat}$, Figure S5) to recalculate the anthropogenic fossil CH_4 emissions ($Q_{Fos,Anthro}$). We use the same CH_4 inventory¹ as was used in the $^{14}CH_4$ box model and the atmospheric $\delta^{13}CH_4$ history for 1988-2013 from ref.⁸⁷, converted into the isotopic history of the CH_4 source ($\delta^{13}C_Q$) by Equation 7 in the supplementary information of ref.³. We use the fractionation factor (ϵ , -6.85, with assumed 1σ uncertainty of $\pm 0.8\%$) from ref.⁸⁷ as this

includes the highly fractionating marine boundary layer atomic chlorine sink mechanism⁸⁸ that was not incorporated within the fractionation factor used in ref. ³ ($-6.3 \pm 0.6\%$, 1σ).

The remaining model parameters are taken from Table 1 in the supplementary information of ref. ³: lifetime (9.0 ± 0.32 years), Biomass burning source (Q_{BMB} , 43 ± 9 Tg CH_4 /yr), soil sink (Q_{soil} , -32 ± 2 Tg CH_4 /yr), and isotopic signatures of Fossil ($\delta^{13}C_{Fos}$, $-44 \pm 0.66\%$) Biomass Burning ($\delta^{13}C_{BMB}$, $-22.35 \pm 1.83\%$) and Microbial ($\delta^{13}C_{Mic}$, $-62.2 \pm 0.78\%$) CH_4 sources. All errors listed represent a $\pm 1\sigma$ normally distributed error about the mean, converted from the median and 10th – 90th percentile limits reported in ref ³. We performed 100,000 iterations in a Monte Carlo analysis, simultaneously solving Equations 16 and 17 for the anthropogenic fossil CH_4 source ($Q_{Fos,Anthro}$) and the Microbial CH_4 source (Q_{Mic}).

$$Q_{Tot} = Q_{Mic} + Q_{Fos,Nat} + Q_{Fos,Anthro} + Q_{BMB} + Q_{Soil} \quad (16)$$

$$\begin{aligned} \delta^{13}C_Q \cdot Q_{Tot} = \\ \delta^{13}C_{Mic} \cdot Q_{Mic} + \delta^{13}C_{Fos} \cdot (Q_{Fos,Nat} + Q_{Fos,Anthro}) + \delta^{13}C_{BMB} \cdot Q_{BMB} \end{aligned} \quad (17)$$

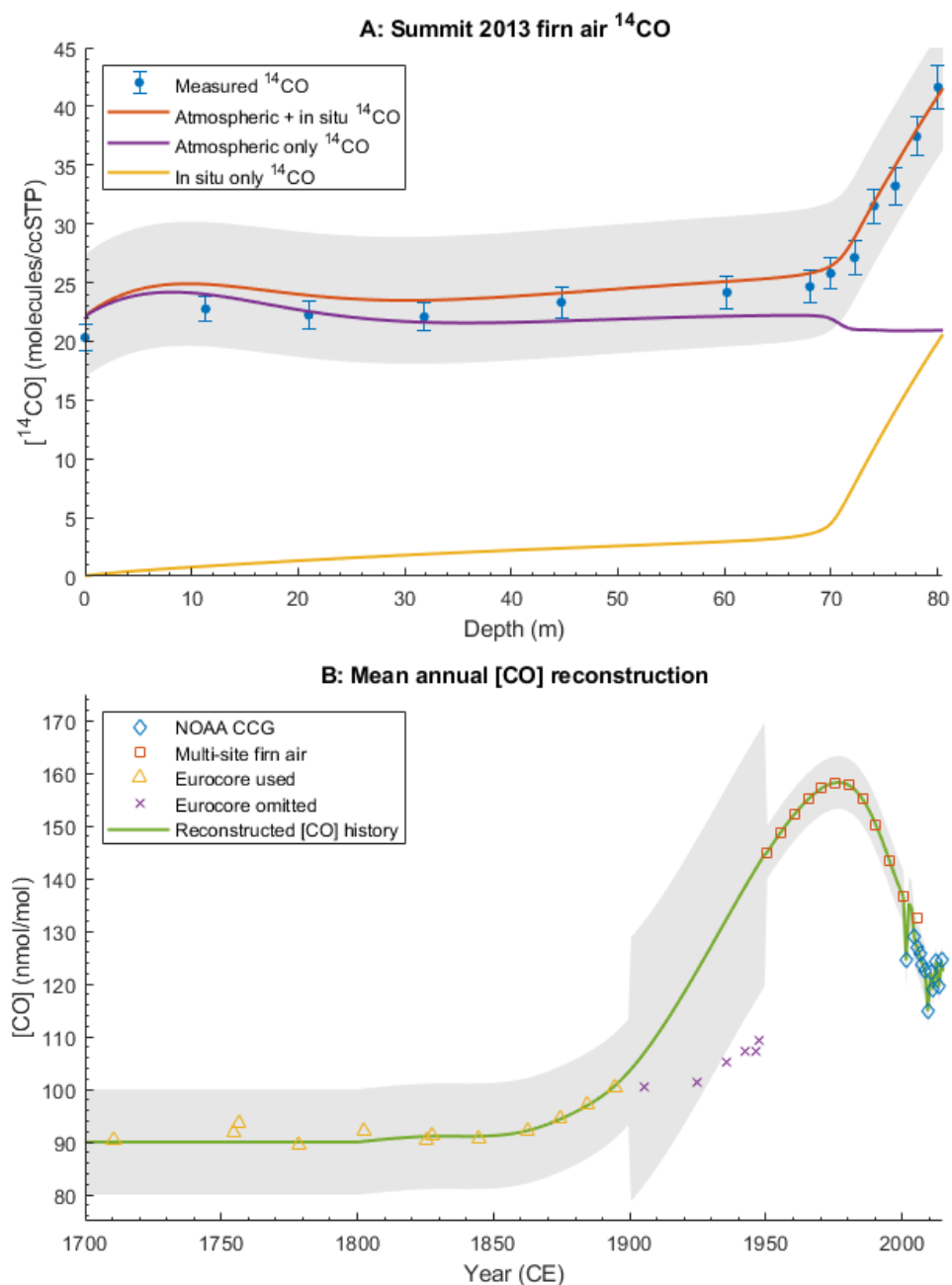


Figure S1:

A: Summit 2013 Firn Air ^{14}CO after correction for extraneous ^{14}C (blue circles with $\pm 1\sigma$ error) and results from forward firn air model. Firn model optimized ^{14}CO profile (red trace) is shown alongside model runs with $\pm 25\%$ uncertainty in the paleoatmospheric ^{14}CO history (grey shading). Also shown are the paleoatmospheric (purple) and in situ cosmogenic (yellow) components of the optimized profile. B: Reconstruction of NH mean annual [CO] (green trace) and $\pm 1\sigma$ uncertainty (grey shading). Also shown are the source data used to develop the reconstruction: ice core measurements from Eurocore (Yellow triangles and purple x's)^{60,61}, a compilation reconstructed from firn air at NEEM, Summit and NGRIP (red squares, shown at 5 year resolution)⁶² and mean annual flask measurements at Summit (blue diamonds)⁶³.

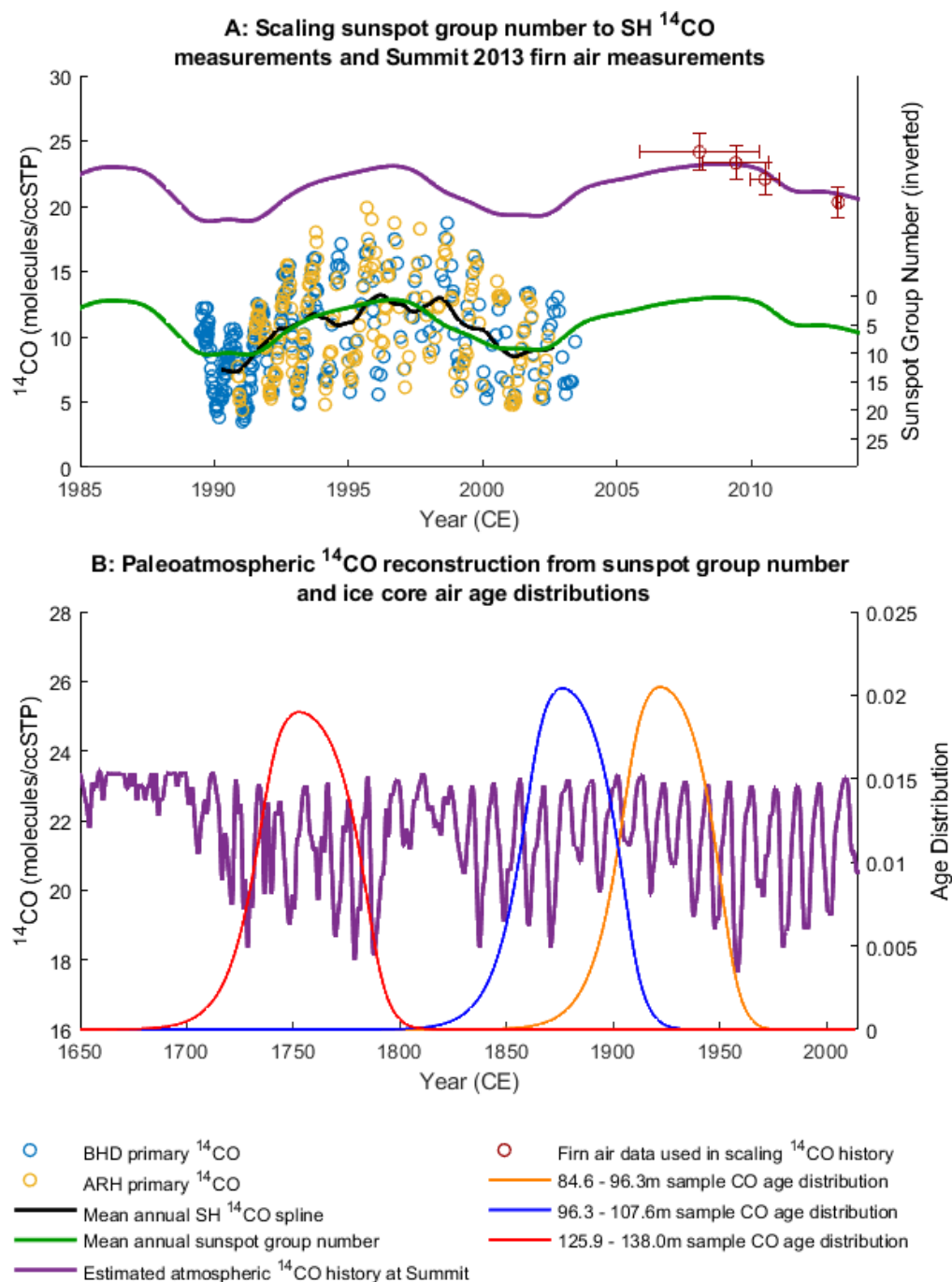


Figure S2:

A: Comparison between Sunspot group number (green trace, right axis)⁵⁷ and primary atmospheric ^{14}CO measurements (left axis) from Baring Head (BHD, blue circles), New Zealand and Arrival Heights (ARH, yellow circles), Antarctica⁵⁶. A constant offset of 10.23 molecules/ccSTP is applied to the spline fit of regression of the mean annual ^{14}CO (black trace) and sunspot group number (green trace) to match the Summit 2013 firn air ^{14}CO measurements that are not significantly affected by seasonal fluctuations and in situ cosmogenic production (red circles). This results in the reconstructed paleoatmospheric ^{14}CO at Summit (purple trace) B: Paleoatmospheric ^{14}CO reconstruction from sunspot group number for 1650 - 2015 and air age distributions for CO in the three ice core samples collected at Summit.

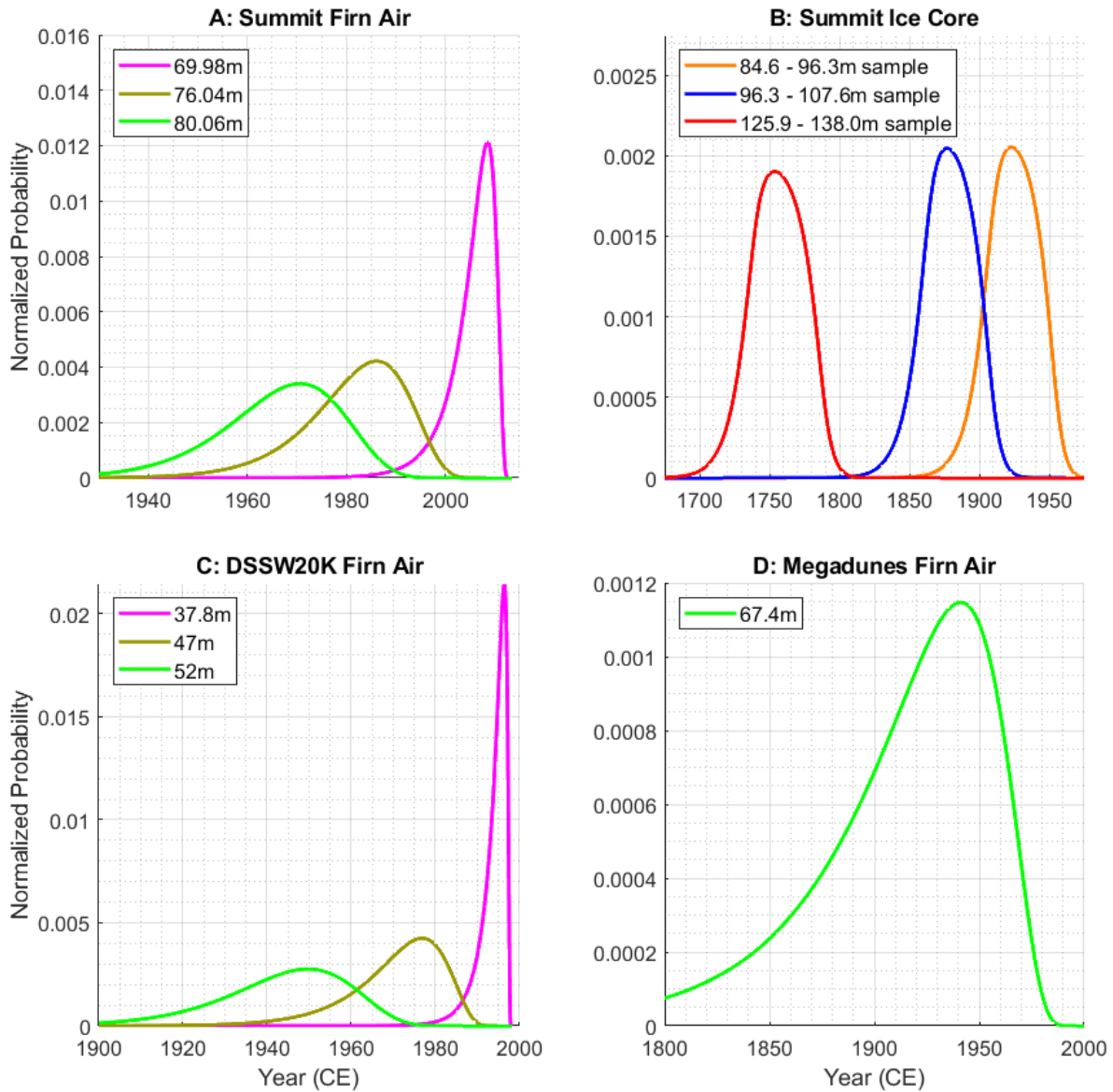


Figure S3:

CH₄ age distributions in firn air and ice core samples. For Summit (A) and DSSW20K (C), three traces are shown illustrating the age distributions in the open porosity at the top, middle and bottom of the LIZ (pink, brown and green respectively). For Megadunes (D) we show the open porosity age distribution at the only depth where we have samples (at the bottom of the LIZ). For the deep ice cores at summit (B), we show the average CH₄ age distribution of the closed porosity considering the entire depth range spanned by each sample.

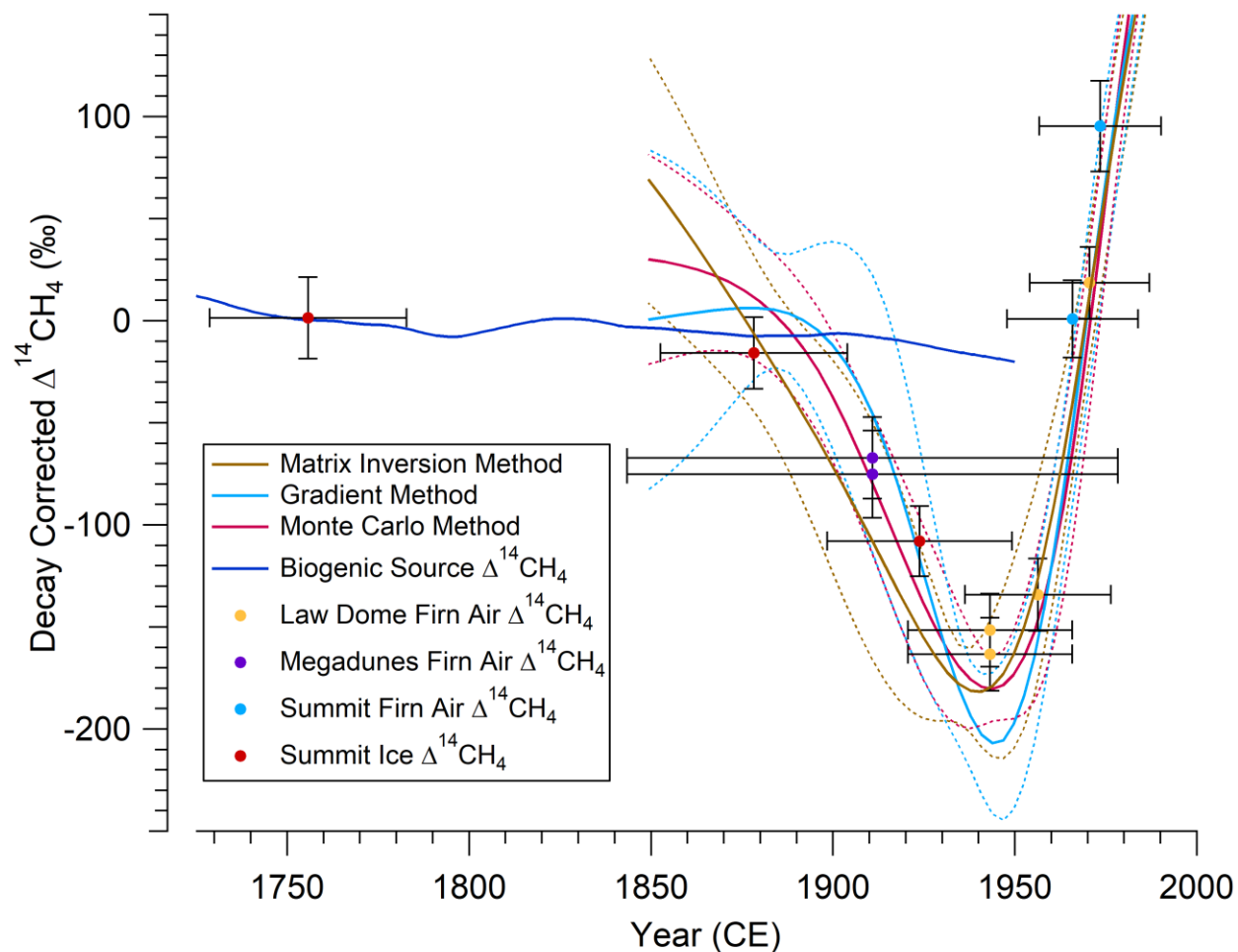


Figure S4:

Continuous reconstruction of atmospheric $\Delta^{14}\text{CH}_4$ separated by method with dotted lines representing 95% confidence interval ranges of all reconstructions for a given method. The range is restricted from Figure 1 in the main text to zoom in on the preindustrial era and early 20th century segments of the reconstruction.

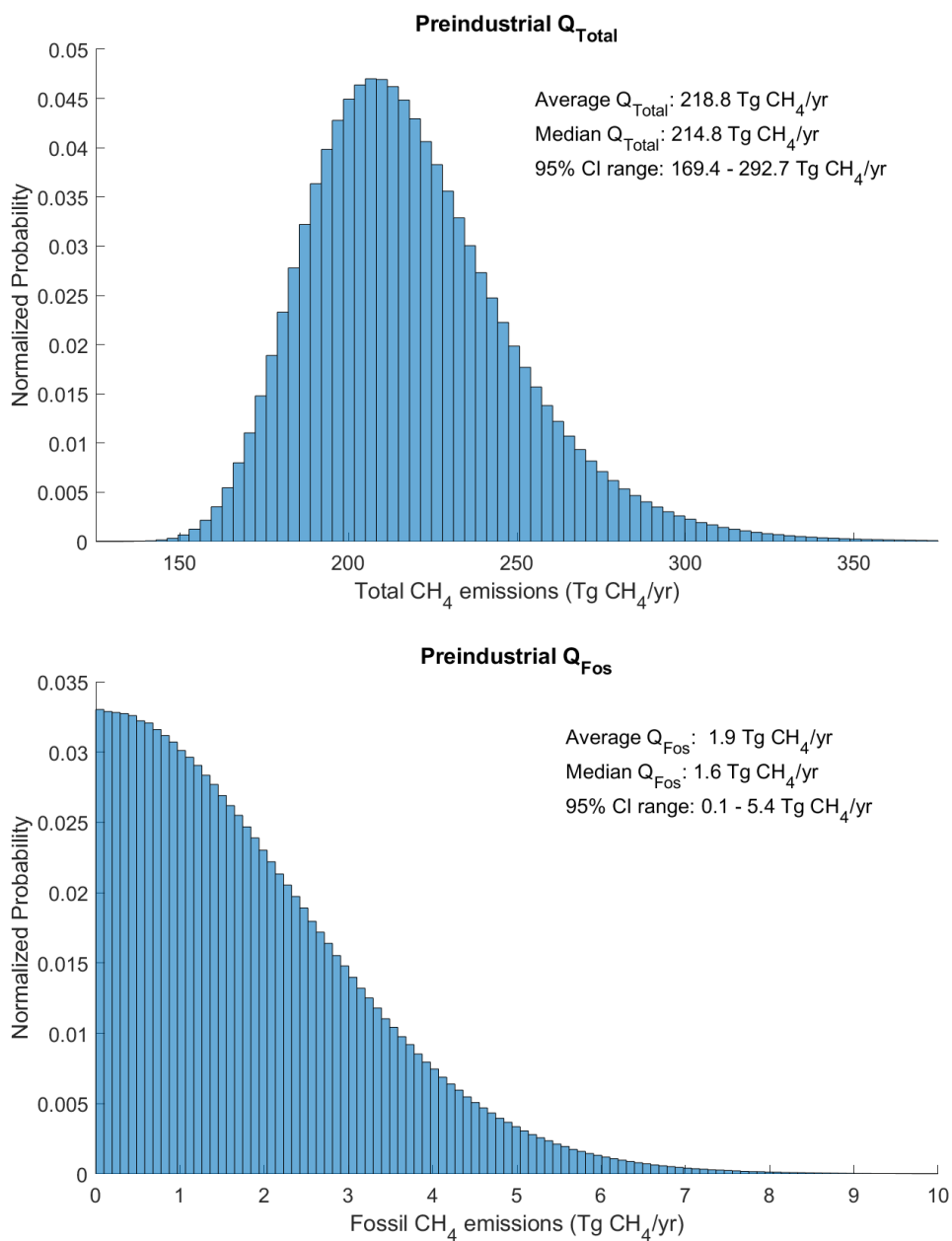


Figure S5:

Probability distributions of (top) total CH_4 emissions and (bottom) natural fossil CH_4 emissions in the preindustrial era calculated from the 1-box model (Supplementary Information Section 10).

Sample Name	CH ₄ Mean age from firn air model (Year CE)	Measured Depths			Depths converted to 2013 firn model depth scale		
		Top Depth (m)	Mean Depth (m)	Bottom Depth (m)	Top Depth (m)	Mean Depth (m)	Bottom Depth (m)
~90m sample	1923.8	85.5 ± 0.2	91.1	96.7 ± 0.3	84.6	90.4	96.3
~100m sample	1878.3	96.7 ± 0.3	102.1	107.5 ± 0.4	96.3	101.9	107.6
~130m sample	1755.8	124.7 ± 0.2	130.3	135.8 ± 0.2	125.9	132	138

Sample Name	Number of Melt extractions performed	Total mass of ice melted (kg)	Total air collected (L STP)	Air content after all corrections (ccSTP/kg)
~90m sample	2	771.99 ± 3.21	65.3 ± 0.8	84.5 ± 1.1
~100m sample	2	789.70 ± 3.21	68.2 ± 0.8	86.4 ± 1.1
~130m sample	3	1190.07 ± 3.93	102.8 ± 1.2	86.3 ± 1.1

Table S1:

Ice Core ¹⁴CH₄ sample Depths and sampling parameters. Depth uncertainty reflects the full range of measured depths from the parallel boreholes. Remaining uncertainties are 1σ, representative of the measurement precision.

Site	Depth (m)	Mean age from firn air model (Year CE)	Measured [CH ₄] (nmol/mol)	Measured ¹⁴ CH ₄ (with δ ¹³ C normalization) (pMC)	¹⁴ CH ₄ after extraneous C correction (pMC)	In situ cosmogenic ¹⁴ CH ₄ content		Final ¹⁴ CH ₄ after all corrections	
						(molecules/ ccSTP)	pMC	pMC	(Age-corrected Δ ¹⁴ C, ‰)
Summit	0	2013.4	1893.2 ± 9.5	137.3 ± 1.1	138.1 ± 1.4			138.1 ± 1.4	370.7 ± 13.9
Summit	11.32	2012.6	1886.8 ± 9.5	136.8 ± 0.8	137.6 ± 1.2	0.006 ± 0.006	0.01 ± 0.01	137.6 ± 1.2	365.5 ± 11.9
Summit	20.99	2011.9	1879.4 ± 9.4	137.1 ± 0.7	137.9 ± 1.1	0.010 ± 0.010	0.02 ± 0.02	137.9 ± 1.1	368.3 ± 11.2
Summit	31.83	2011.0	1871.9 ± 9.4	137.3 ± 0.7	138.1 ± 1.1	0.014 ± 0.014	0.03 ± 0.03	138.1 ± 1.1	371.0 ± 11.4
Summit	44.69	2010.0	1865.1 ± 9.4	135.4 ± 0.6	136.1 ± 1.0	0.018 ± 0.018	0.03 ± 0.03	136.1 ± 1.0	351.3 ± 10.5
Summit	60.25	2008.8	1856.4 ± 9.3	136.0 ± 0.7	136.8 ± 1.1	0.022 ± 0.022	0.04 ± 0.04	136.7 ± 1.1	357.7 ± 11.2
Summit	68.02	2007.3	1851.2 ± 9.3	138.1 ± 1.1	138.9 ± 1.4	0.027 ± 0.024	0.05 ± 0.04	138.9 ± 1.4	379.1 ± 13.8
Summit	69.98	2005.3	1837.7 ± 9.2	135.4 ± 0.8	136.2 ± 1.2	0.034 ± 0.023	0.06 ± 0.04	136.2 ± 1.2	352.6 ± 11.9
Summit	72.21	1997.1	1809.5 ± 9.1	131.7 ± 0.7	132.4 ± 1.1	0.059 ± 0.023	0.11 ± 0.04	132.3 ± 1.1	315.6 ± 10.8
Summit	74.05	1989.3	1740.9 ± 8.8	123.3 ± 0.7	124.0 ± 1.0	0.083 ± 0.023	0.16 ± 0.04	123.9 ± 1.0	232.7 ± 10.2
Summit	76.04	1981.2	1666.8 ± 8.3	116.5 ± 1.2	117.1 ± 1.4	0.107 ± 0.024	0.22 ± 0.05	116.9 ± 1.4	164.7 ± 14.0
Summit	78.03	1973.4	1568.5 ± 7.9	109.5 ± 0.8	110.1 ± 1.1	0.130 ± 0.024	0.29 ± 0.05	109.8 ± 1.1	94.9 ± 11.1
Summit	80.06	1965.8	1434.1 ± 7.2	100.1 ± 0.6	100.6 ± 0.9	0.152 ± 0.025	0.36 ± 0.06	100.3 ± 0.9	0.8 ± 9.4
DSSW20K	0	1998.1	1706.1 ± 10	128.8 ± 1	128.4 ± 1.1			128.4 ± 1.1	276.1 ± 11
DSSW20K	29	1995.0	1691.9 ± 10	124.9 ± 1	124.5 ± 1.1	0.008 ± 0.008	0.02 ± 0.02	124.5 ± 1.1	237.8 ± 11
DSSW20K	37.8	1993.7	1680.4 ± 10	123.5 ± 1	123.1 ± 1.1	0.011 ± 0.011	0.02 ± 0.02	123.1 ± 1.1	224.3 ± 11
DSSW20K	41.7	1992.8	1660.0 ± 10	123.6 ± 1	123.2 ± 1.1	0.014 ± 0.014	0.03 ± 0.03	123.1 ± 1.1	225 ± 11
DSSW20K	44.5	1985.1	1584.2 ± 10	117.1 ± 1	116.7 ± 1.1	0.031 ± 0.015	0.06 ± 0.03	116.6 ± 1.1	161.1 ± 11
DSSW20K	47	1970.5	1366.4 ± 10	102.7 ± 1	102.3 ± 1.1	0.063 ± 0.031	0.15 ± 0.08	102.1 ± 1.1	18.5 ± 11
DSSW20K	49.5	1956.3	1188.7 ± 12	87.3 ± 1	86.9 ± 1.1	0.094 ± 0.047	0.26 ± 0.13	86.6 ± 1.1	-134.3 ± 11
DSSW20K	52	1943.1	1082.2 ± 12	84.4 ± 1	83.9 ± 1.1	0.122 ± 0.061	0.37 ± 0.19	83.6 ± 1.1	-163.6 ± 11.1
DSSW20K	52	1943.1	1084.1 ± 12	85.6 ± 1	85.1 ± 1.1	0.122 ± 0.061	0.37 ± 0.19	84.7 ± 1.1	-151.8 ± 11.1
Megadunes	67.4	1910.9	938.3 ± 8	94.5 ± 0.5	93.8 ± 0.7	0.326 ± 0.163	1.11 ± 0.55	92.6 ± 0.9	-69.1 ± 8.8
Megadunes	67.4	1910.9	938 ± 8	93.7 ± 0.6	93 ± 0.8	0.326 ± 0.163	1.11 ± 0.55	91.9 ± 1	-77.1 ± 9.6

Table S2:

Measured firn air [CH₄] and ¹⁴CH₄, including the effects of corrections for extraneous carbon addition and in situ cosmogenic ¹⁴CH₄ production. All errors represent ± 1σ.

Depth	Lab-measured [CO] in glass flasks	Lab-measured [CO] in 35L SS flasks	Percentage of CO carbon from sample after dilution with ^{14}C -depleted gas	Measured ^{14}CO (with $\delta^{13}\text{C}$ normalization)	^{14}CO corrected for dilution		^{14}CO after all procedural corrections	Estimated in situ cosmogenic ^{14}CO
(m)	(nmol/mol)	(nmol/mol)	(%)	(pMC)	(pMC)	(molecules/ccSTP)	(molecules/ccSTP)	(molecules/ccSTP)
0	125.7 $\pm$ 0.5	151.72 $\pm$ 1.91	9.10 $\pm$ 0.45	47.28 $\pm$ 0.45	505.44 $\pm$ 25.57	23.38 $\pm$ 1.15	20.32 $\pm$ 1.16	0 $\pm$ 0
11.32	134.5 $\pm$ 1.5	187.44 $\pm$ 2.50	9.17 $\pm$ 0.39	42.44 $\pm$ 0.36	448.76 $\pm$ 19.39	25.63 $\pm$ 1.06	22.76 $\pm$ 1.08	0.9 $\pm$ 0.9
20.99	126.6 $\pm$ 0.7	153.70 $\pm$ 2.08	9.08 $\pm$ 0.45	49.78 $\pm$ 0.64	534.17 $\pm$ 27.20	25.02 $\pm$ 1.23	22.24 $\pm$ 1.25	1.4 $\pm$ 1.4
31.83	122.4 $\pm$ 1.1	151.98 $\pm$ 1.93	9.10 $\pm$ 0.45	49.95 $\pm$ 0.34	534.85 $\pm$ 26.75	24.77 $\pm$ 1.20	22.09 $\pm$ 1.22	1.9 $\pm$ 1.9
44.69	122.0 $\pm$ 0.5	149.47 $\pm$ 1.87	9.13 $\pm$ 0.46	53.23 $\pm$ 0.35	569.01 $\pm$ 28.88	25.92 $\pm$ 1.28	23.33 $\pm$ 1.29	2.4 $\pm$ 2.4
60.25	122.1 $\pm$ 0.5	142.78 $\pm$ 1.75	9.07 $\pm$ 0.47	56.81 $\pm$ 0.44	612.66 $\pm$ 32.20	26.66 $\pm$ 1.37	24.17 $\pm$ 1.38	3.0 $\pm$ 3.0
68.02	123.9 $\pm$ 0.5	145.34 $\pm$ 3.11	9.11 $\pm$ 0.49	56.94 $\pm$ 0.45	610.92 $\pm$ 33.26	27.06 $\pm$ 1.37	24.65 $\pm$ 1.39	3.6 $\pm$ 3.1
69.98	149.5 $\pm$ 1.0	160.00 $\pm$ 2.26	9.10 $\pm$ 0.44	53.89 $\pm$ 0.38	578.05 $\pm$ 27.97	28.18 $\pm$ 1.31	25.78 $\pm$ 1.33	4.5 $\pm$ 3.0
72.21	136.5 $\pm$ 0.7	156.62 $\pm$ 1.89	9.08 $\pm$ 0.44	57.23 $\pm$ 0.37	616.51 $\pm$ 29.91	29.44 $\pm$ 1.39	27.12 $\pm$ 1.41	7.8 $\pm$ 3.0
74.05	145.0 $\pm$ 0.8	181.46 $\pm$ 3.55	9.09 $\pm$ 0.41	56.90 $\pm$ 0.47	611.84 $\pm$ 28.01	33.84 $\pm$ 1.43	31.53 $\pm$ 1.44	10.9 $\pm$ 3.0
76.04	150.9 $\pm$ 0.5	172.98 $\pm$ 3.09	9.12 $\pm$ 0.42	62.57 $\pm$ 0.47	672.46 $\pm$ 31.42	35.45 $\pm$ 1.55	33.23 $\pm$ 1.57	14.1 $\pm$ 3.0
78.03	149.6 $\pm$ 0.6	181.81 $\pm$ 3.04	9.09 $\pm$ 0.4	66.35 $\pm$ 0.53	715.90 $\pm$ 32.07	39.67 $\pm$ 1.67	37.45 $\pm$ 1.68	17.1 $\pm$ 3.1
80.06	157.7 $\pm$ 5.0	175.04 $\pm$ 2.01	9.08 $\pm$ 0.4	75.74 $\pm$ 0.43	820.09 $\pm$ 36.26	43.75 $\pm$ 1.88	41.62 $\pm$ 1.89	20.0 $\pm$ 3.2
Procedural blank #1		18.99 $\pm$ 1.70	1.32 $\pm$ 0.14	8.16 $\pm$ 0.14	517.41 $\pm$ 56.24	2.96 $\pm$ 0.18		
Procedural blank #2		30.15 $\pm$ 2.69	2.11 $\pm$ 0.22	5.86 $\pm$ 0.12	213.37 $\pm$ 23.44	1.94 $\pm$ 0.12		
^{14}C -depleted standard gas	10290 $\pm$ 130			1.42 $\pm$ 0.08				

Table S3:

Measurement of Summit 2013 firm air [CO] and ^{14}CO and associated corrections. All errors represent $\pm 1\sigma$.

Sample or Blank name	Measured [CH ₄] (nmol/mol)	CH ₄ solubility correction factor ---	Fraction of air in blanks comprised of leftover purge gas ---	Purge gas [CH ₄] (nmol/mol)	[CH ₄] corrected for solubility (samples and blanks) and leftover purge gas (blanks only) (nmol/mol)
~90m sample	1043.11 ± 5.23	0.9701 ± 0.0021			1075.24 ± 5.89
~100m sample	858.69 ± 4.34	0.9677 ± 0.0024			887.33 ± 5.00
~130m sample	736.63 ± 3.78	0.9682 ± 0.0024			760.84 ± 4.33
Procedural Blank #1	383.37 ± 2.01	0.9784 ± 0.0003	0.0214 ± 0.0012	1.7 ± 0.6	400.35 ± 2.14
Procedural Blank #2	1322.78 ± 6.63	0.9647 ± 0.0026	0.0728 ± 0.0016	5.0 ± 0.6	1478.58 ± 9.47
¹⁴ C-depleted CH ₄ Standard	401.95 ± 2.1				
¹⁴ C-modern CH ₄ Standard	1473.6 ± 7.4				

Table S4:

Ice core [CH₄] and stepwise consideration of associated procedural corrections. [CH₄] is not corrected for gravitational fractionation in the firm column, this effect is considered by the firm model. All errors are ±1σ

Sample or Blank name	Measured [CO]	Percentage of CO carbon from sample after dilution with ^{14}C -depleted gas	[CO] after dilution with high-[CO], ^{14}C -depleted standard	CO solubility correction factor	[CO] corrected for Solubility	[CO] corrected for Solubility and procedural effects based on procedural blanks	Further extraneous [CO] not represented by procedural blanks after subtraction of paleoatmospheric [CO]
	(nmol/mol)	(%)	(nmol/mol)	---	(nmol/mol)	(nmol/mol)	(nmol/mol)
~90m sample	304.21 $\pm$ 1.02	7.14 $\pm$ 0.17	3076.07 $\pm$ 57.37	0.9916 $\pm$ 0.0006	306.80 $\pm$ 1.04	228.42 $\pm$ 21.50	105.79 $\pm$ 30.97
~100m sample	284.03 $\pm$ 0.98	4.50 $\pm$ 0.09	3979.30 $\pm$ 60.78	0.9909 $\pm$ 0.0007	286.63 $\pm$ 1.01	208.28 $\pm$ 21.49	111.44 $\pm$ 24.49
~130m sample	279.23 $\pm$ 0.99	6.60 $\pm$ 0.16	3057.53 $\pm$ 57.40	0.9910 $\pm$ 0.0007	281.78 $\pm$ 1.02	203.25 $\pm$ 21.50	113.18 $\pm$ 23.66
Procedural Blank #1	56.62 $\pm$ 0.95	2.38 $\pm$ 0.09	1942.34 $\pm$ 58.80	0.9941 $\pm$ 0.0002	56.96 $\pm$ 0.96		
Procedural Blank #2	98.88 $\pm$ 0.95	1.90 $\pm$ 0.04	3482.02 $\pm$ 59.43	0.9902 $\pm$ 0.0008	99.86 $\pm$ 0.96		
^{14}C -depleted CO Standard	10290 $\pm$ 130						

Table S5:

Ice core [CO] and stepwise consideration of associated procedural corrections. [CO] is not corrected for gravitational fractionation in the first column, this effect is considered by the firn model. All errors are $\pm 1\sigma$

Sample or Blank name	Measured $^{14}\text{CH}_4$	$^{14}\text{CH}_4$ after procedural corrections	In situ cosmogenic $^{14}\text{CH}_4$ content		Final corrected paleoatmospheric $^{14}\text{CH}_4$	
	(pMC)	(pMC)	(molecules/g ice)	(pMC)	(pMC)	(Age-corrected $\Delta^{14}\text{C}$, ‰)
~90m sample	89.31 ± 0.65	89.66 ± 0.86	0.0194 ± 0.0020	0.72 ± 0.08	88.94 ± 0.86	-107.73 ± 8.85
~100m sample	98.32 ± 0.64	98.77 ± 0.88	0.0266 ± 0.0022	1.16 ± 0.10	97.60 ± 0.88	-15.45 ± 9.14
~130m sample	99.07 ± 0.78	99.53 ± 1.00	0.0334 ± 0.0025	1.70 ± 0.13	97.83 ± 1.01	1.54 ± 10.60
Procedural Blank #1	1.20 ± 0.10					
Procedural Blank #2	135.06 ± 0.84					
Modern $^{14}\text{CH}_4$ Standard	135.67 ± 0.44					
Dead $^{14}\text{CH}_4$ Standard	0.53 ± 0.06					

Table S6:

Ice core $^{14}\text{CH}_4$ measurements and effects of procedural corrections & in situ cosmogenic $^{14}\text{CH}_4$. Final corrected $^{14}\text{CH}_4$ values do not include corrections for gravitational and diffusive fractionation in the firn column; both of which are accounted for by the firn models. All errors are $\pm 1\sigma$

Sample or Blank name	Measured ^{14}CO	^{14}CO corrected for dilutions		^{14}CO further corrected for procedural blank	Estimated paleoatmospheric ^{14}CO content	Extraneous ^{14}CO not captured by procedural blanks	^{14}CO further corrected for Melting blank and bubble air	In situ Cosmogenic ^{14}CO
	(pMC)	(pMC)	(molecules/ccSTP)	(molecules/ccSTP)	(molecules/ccSTP)	(molecules/ccSTP)	(molecules/ccSTP)	(molecules/gIce)
~90m sample	53.43 ± 0.63	726.45 ± 19.51	67.29 ± 1.79	52.56 ± 1.94	20.77 ± 1.97	1.63 ± 0.83	30.16 ± 2.89	2.55 ± 0.25
~100m sample	41.85 ± 0.65	894.56 ± 22.84	77.31 ± 1.96	62.72 ± 2.09	20.50 ± 1.96	1.72 ± 0.80	40.50 ± 2.99	3.50 ± 0.26
~130m sample	69.23 ± 0.56	1025.86 ± 26.08	87.22 ± 2.20	72.72 ± 2.32	19.41 ± 1.93	1.75 ± 0.80	51.01 ± 3.20	4.40 ± 0.28
Procedural Blank #1	23.09 ± 0.29	903.13 ± 38.02	15.54 ± 0.60					
Procedural Blank #2	10.99 ± 0.32	493.32 ± 20.72	14.83 ± 0.61					
Dead ^{14}CO Standard	1.66 ± 0.07							

Table S7:

Ice core ^{14}CO measurements and effects of procedural corrections & in situ cosmogenic $^{14}\text{CH}_4$. Final corrected ^{14}CO values do not include corrections for gravitational and diffusive fractionation in the firn column; both of which are accounted for by the firn models. All errors are $\pm 1\sigma$

Input parameter	Resulting $Q_{\text{Fos,Nat}}$ (in Tg CH ₄ /yr) by setting input parameter equal to its lower 95% CI limit	Resulting $Q_{\text{Fos,Nat}}$ (in Tg CH ₄ /yr) by setting input parameter equal to its upper 95% CI limit
	Median (95% CI Range)	Median (95% CI Range)
Atmospheric CH ₄ Burden (M_{CH_4})	1.5 (0.1 - 5.3)	1.6 (0.1 - 5.5)
Atmospheric Lifetime (τ)	2.1 (0.1 - 7.0)	1.2 (0.1 - 4.1)
Biogenic source signature ($\Delta^{14}\text{CH}_4$, Bio Source)	1.1 (0.0 - 4.2)	2.2 (0.1 - 6.3)
In situ cosmogenic correction	1.5 (0.1 - 5.1)	1.7 (0.1 - 5.7)
AMS Measurement precision on ^{14}C for the Preindustrial era sample	3.6 (0.6 - 7.0)	0.2 (0.0 - 1.2)
Procedural corrections for $\Delta^{14}\text{CH}_4$	2 (0.1 - 5.8)	1.2 (0.0 - 4.3)
Best estimate value with no perturbations:	1.6 (0.1 - 5.4)	

Table S8:

Error sensitivity analysis for the box model calculation of preindustrial era fossil CH₄ emissions ($Q_{\text{Fos,Nat}}$). For each of the listed calculations, the highlighted input parameter was set to a constant value equal to the upper (or lower) 95% CI limit for that parameter. All other parameters in the calculation were still allowed to vary within their uncertainties. Resulting median and 95% CI are given for each case. The best estimate values are also shown for comparison.

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