Supplementary Information

Local artifacts in ice core methane records caused by layered bubble trapping and in-situ production: a multi-site investigation

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1. Additional information about processing of the continuous CH_4 data

Methane concentrations measured by the SARA laser spectrometer were transferred to the NOAA2004 scale by measuring three NOAA-certified reference gases (CA04382 = 385 ppb, CA04332 = 667 ppb and CC302559 = 1853 ppb). Measurements conducted in September 2013 were calibrated using equation 1.

$$CH_{4NOAA2004} = 1.0127*CH_{4meas.} - 1.4201 \quad (1)$$

Measurements conducted in October 2013 were calibrated using equation 2.

$$CH_{4NOAA2004} = 0.9878*CH_{4meas.} + 5.0957 \quad (2)$$

Different calibrations were applied in September and October because maintenance was carried out on the instrument between measurement sessions. Please see Table S1 for analysis dates.

NOAA-calibrated methane concentrations were corrected for dissolution in the liquid phase using measurements made on a synthetic sample mixture of reference gas and degassed water as described previously (Rhodes et al., 2015, 2013). Each core or analytical batch has a unique solubility correction to account for differences in system parameters, particularly melt rate and degasser used (Table S1).

2. Modifications to Oregon State University (OSU) discrete CH_4 analysis

A minor change to the methods reported by Mitchell et al. (2011) relates to the application of solubility and blank corrections to discrete CH_4 measurements conducted at OSU. As detailed by Mitchell et al. (2011), the blank correction is determined by adding a known pressure of standard gas over ultra pure air-free ice (AFI). The measured deviation in CH_4 concentration from a calibrated standard gas (500.22 ppb) comprises the

blank correction. The solubility correction (SC) is determined by performing a secondary melt-refreeze cycle. The high solubility of CH_4 relative to N_2 results in a CH_4 depletion in the the measured sample. We have modified how these corrections are applied. Previously, corrected CH_4 ($CH_{4\ cor}$) values were calculated using equation 3.

$$CH_{4\ cor} = (CH_{4\ sample} - CH_{4\ blank}) * SC \quad 3)$$

This calculation underestimates the solubility effect on the blank, and therefore ultimately also underestimates $CH_{4\ cor}$. The revised calculation fully accounts for the solubility effect on the blank and sample measurements (eq. 4).

$$CH_{4\ cor} - (CH_{4\ sample} * SC - CH_{4\ AFI}) * -CH_{4\ standard} \quad 4)$$

$CH_{4\ AFI}$ values on the OSU system are typically 505 ppb, meaning that measurements corrected using equation 4 (as this study) are 8.5 ppb higher than those corrected using equation 3.

3. Splicing of Tunu13 Main and Tunu13 B records

Ice from Tunu13 B core was analysed instead of Tunu13 Main core for sections with poor Main core quality. Tunu13 B core CH_4 and chemistry data are spliced into the Tunu13 Main record for the following depth ranges: 139.9–136.3 m, 131.5–128.6 m, 128.0–120.4 m & 105.2–99.63 m. Comparison between Tunu13 Main and B chemistry records suggested that there was a 40 cm depth offset between the two cores. All Tunu13 B core depths were increased by 40 cm before splicing the CH_4 and chemistry data into the Tunu13 Main record.

4. Calculation of peak-to-peak amplitude

The peak-to-peak amplitude of the high frequency CH_4 residual was calculated using a publically available Matlab function called Peakdet (eq. 5).

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[MAXTAB, MINTAB] = PEAKDET(V, DELTA)
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5)

This function finds the local minima and maxima in the vector V. A data point is considered to be a maximum if it is the highest value and was preceded by a values lower by >=DELTA. DELTA is set to 2 ppb, slightly greater than the 2σ internal precision.

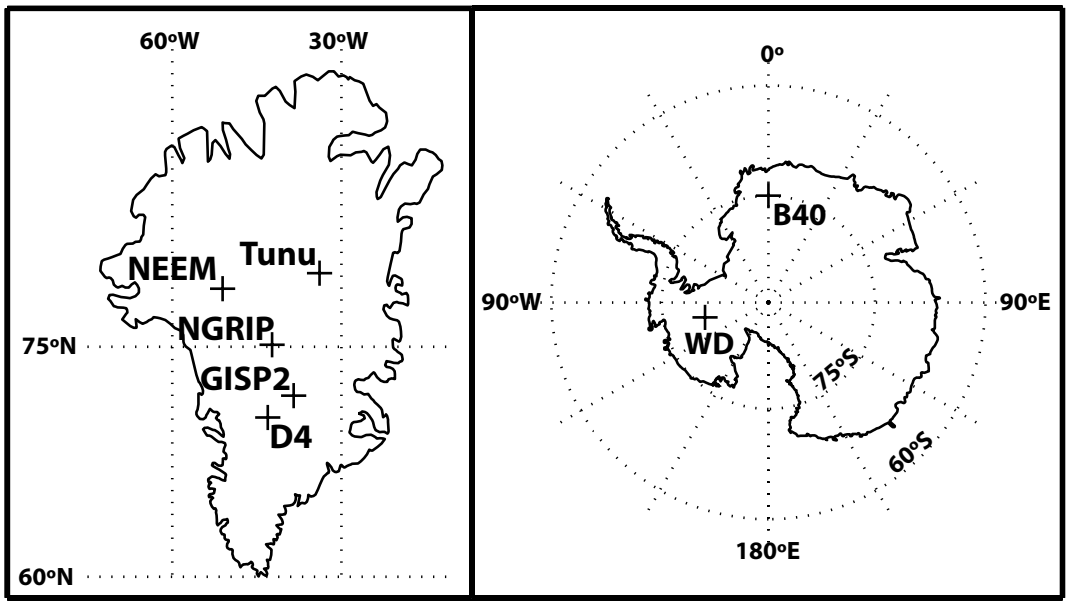

Figure S1: Locations of ice cores analyzed in study or referred to in the text. Greenland on left panel: Tunu(13) (78.035ºN, 33.879ºW), 2,200 m elevation; North Greenland Eemian (NEEM) (77.45ºN, 51.06ºW), elevation 2,450 m; North Greenland Ice Sheet Project (NGRIP) (75.10ºN, 42.32ºW), elevation 2,917 m; Greenland Ice Sheet Project 2 (GISP2) (72.60ºN, 38.5ºW), 3207 m elevation; D4 (71.40ºN, 43.08ºW), elevation 2,713 m. Antarctica on right panel: B40 (75.001ºS, 0.068ºE) , 2911 m elevation, West Antarctic Ice Sheet Divide (WD) (79.47ºS, 112.08ºW), 1766 m elevation.

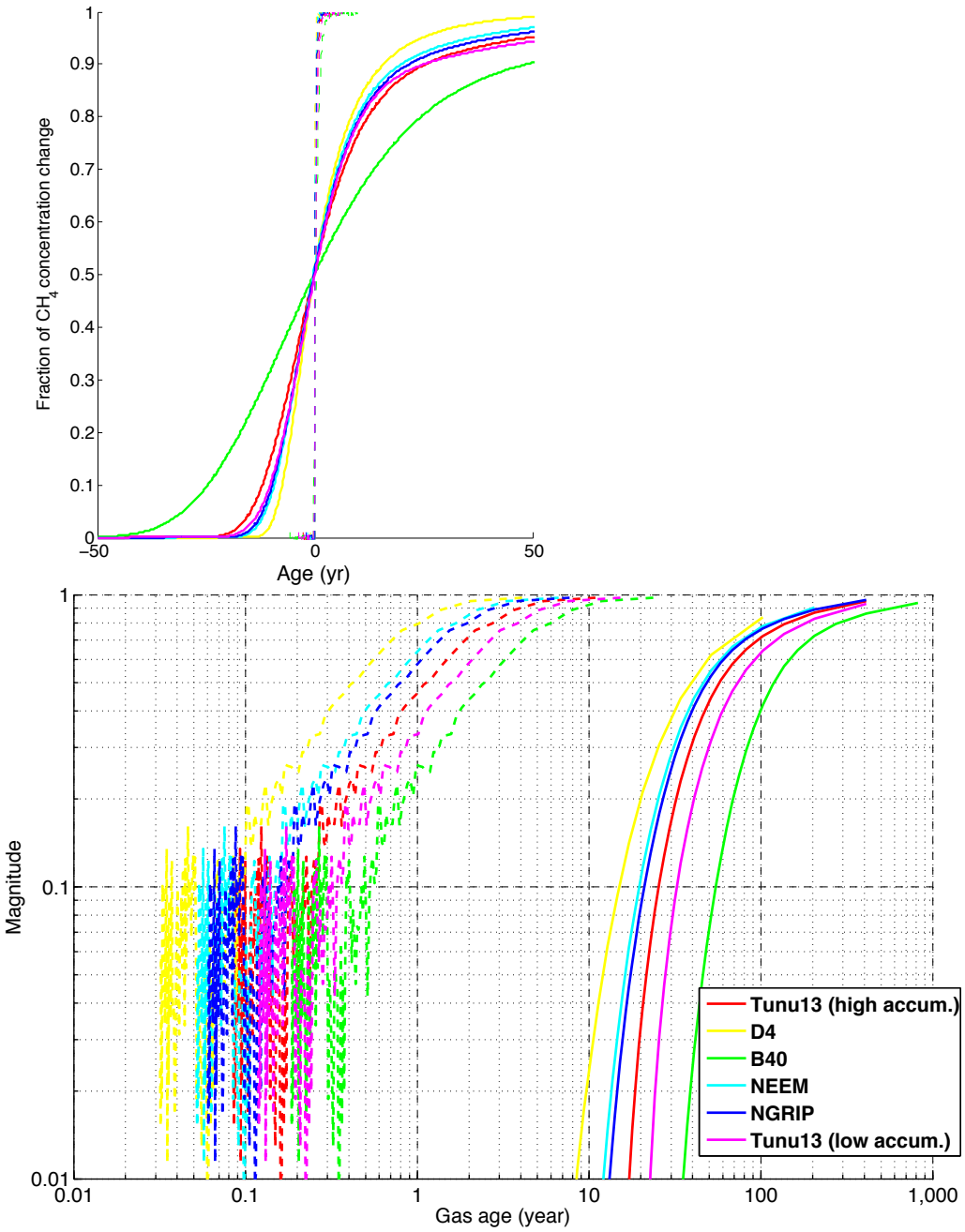

Figure S2: Upper panel) Relative smoothing of the analytical system (dashed lines) and firn-based processes (solid line) for each ice core (see legend). Lower panel) Bode magnitude plot showing magnitude of frequency response to filters representative of analytical system and firn smoothing for different ice cores. If we assume that CH_4 variability is present in the ice cores at a 1 yr periodicity, the fraction of the original amplitude of that signal remaining after damping by the analytical system can be estimated

from this figure as: 0.4 for Tunu13 high accumulation, 0.8 for D4, 0.2 for B40, 0.65 for NEEM, 0.57 for NGRIP and 0.35 for Tunu13 low accumulation.

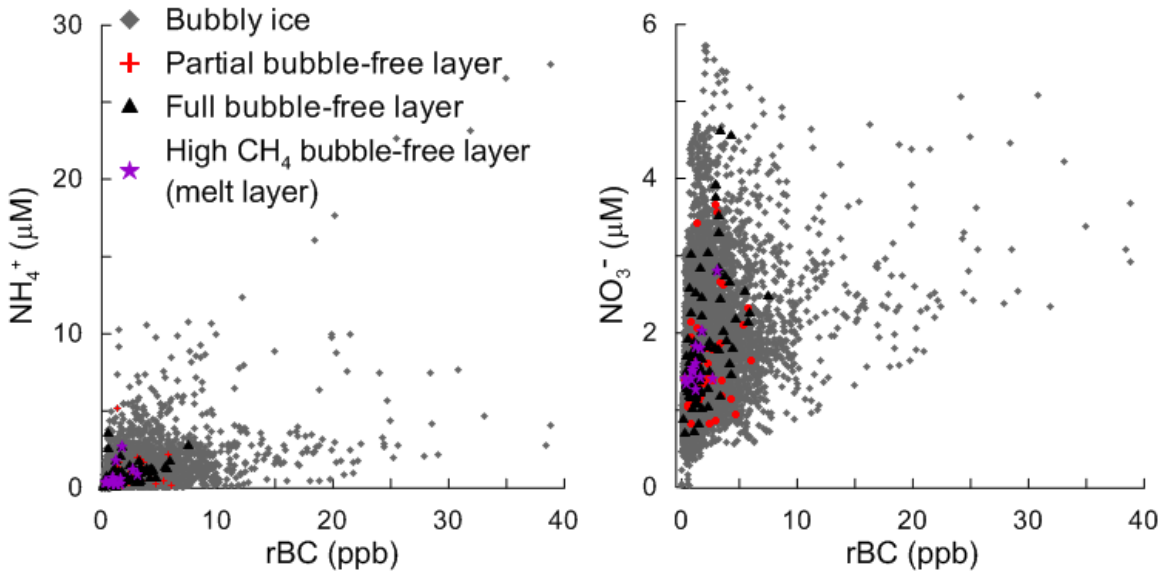

Figure S3: Bi-plots to compare chemical concentrations in Tunu13 ice core at depths coincident with a full bubble-free layer (present across the melter stick surface area), partial bubble-free layer (present across part of melter stick surface area), bubble-free layers with anomalously high CH_4 (continuous and discrete data) concentrations, and depths of bubbly ice with no observed layers. Refractory black carbon (rBC), nitrate (NO_3^-) and ammonium (NH_4^+) are plotted. Bubble-free layers may be melt layers or wind crusts and it is difficult to distinguish between the two by eye.

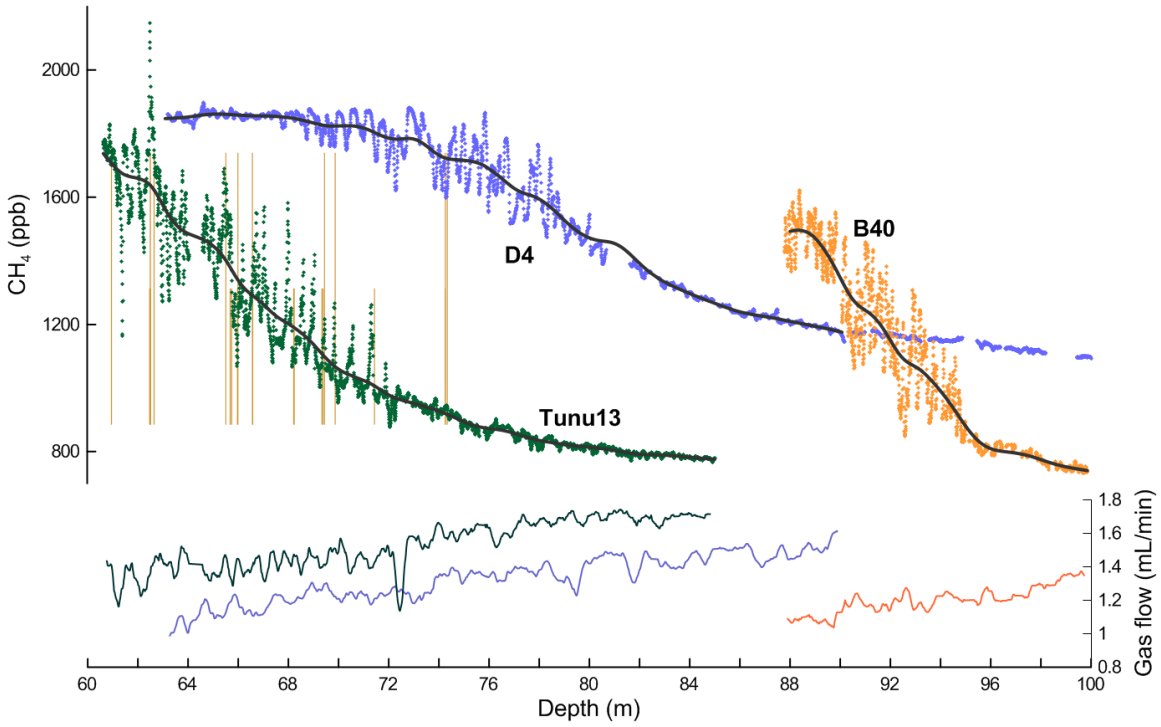

Figure S4: Lock-in zone CH_4 data for Tunu13 (green), D4 (violet) and B40 (orange) with cubic spline fits (black). Gas sample flow recorded by the laser spectrometer is also shown for each core. Vertical brown lines through Tunu13 data show position of melt layers. Abrupt increase in amplitude of signal variability indicates location of close-off depth in each core.

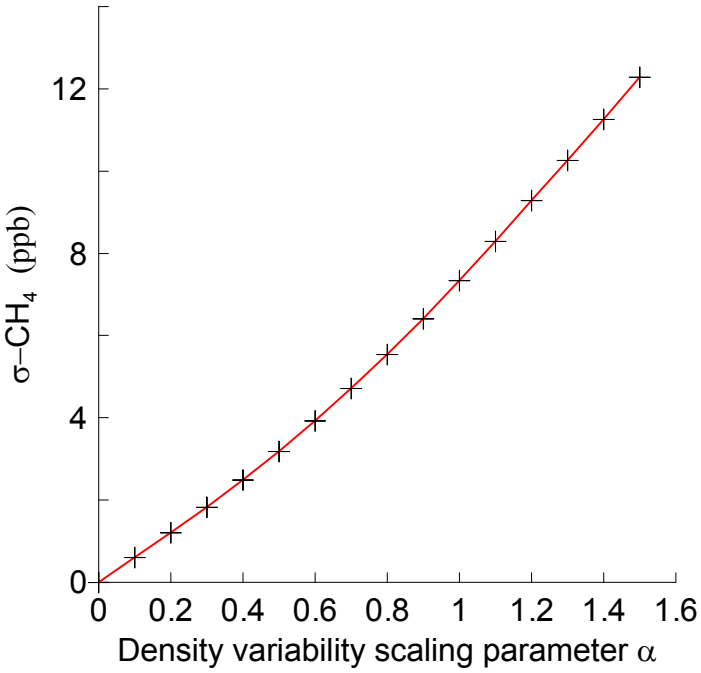

Figure S5: Relationship between magnitude of density variability (α) and high frequency CH_4 variability (σ-CH_4) as predicted by the CIC firn air transport model for the WAIS Divide ice core. The scaling factor (α) applied to the WAIS Divide high resolution density information used by the model is varied between 0 and 1.6. When α=1 the density is not modified. A growth rate of 2.5 ppb yr^{-1} and an accumulation rate of 0.22 m (ice) yr^{-1} are assumed.

Table S1: Online system operating parameters and system performance. Please refer to footnotes for explanation.

Ice core	Analysis dates	Depth interval (m)	Mean melt rate (cm/min)	Mean (gas) sample flow (sccm)	Melter-head	De-gasser	System response time (cm)	Solubility correction	Breaks/m (mean ± s.d)**
B40	11-13/09/13	200–122	5.54	1.59	Standard	M	9.4	$CH_4cor=(7^{-6}*CH_{4NOAA}^2)+(1.086*CH_{4NOAA})$	1.4 ± 0.4
	16-17/09/13	122–88	5.54	1.30	Standard	IL		$CH_4cor=(2^{-5}*CH_{4NOAA}^2)+(1.085*CH_{4NOAA})$	
	18/09/13	157–148	5.86	1.35	Standard	IL			
D4*	7-9/08/13	146–61	7.62	1.54	Small	M	13.0	$CH_4cor=1.1062*CH_{4NOAA}$	0.6 ± 0.3
	15/08/13	145–123		1.54	Small	M			
NEEM	3-6/09/13	573–491, 444–399	5.70	1.88	Standard	M	9.7	$CH_4cor=(1^{-5}*CH_{4NOAA}^2)+(1.069*CH_{4NOAA})$	1.9 ± 0.7
	7-8/10/13	491–444	5.70	1.76	Standard	IL		$CH_4cor=(4^{-6}*CH_{4NOAA}^2)+(1.114*CH_{4NOOAA})$	
NGRIP	30/09-4/10/13	254–207, 108–91 569–519	5.72	1.37	Dual ring Dual ring	IL IL	9.7	$CH_4cor=(1^{-5}*CH_{4NOAA}^2)+(1.119*CH_{4NOOAA})$	2.1 ± 0.6
	08/31/13	91–74			Standard	IL			
Tunu13	13-21/08/13	213–73	5.94	1.8	Standard	M	10.1	$CH_4cor=(1^{-5}*CH_{4NOAA}^2)+(1.069*CH_{4NOAA})$	1.6 ± 1.6

* Only D4 data analysed on 07/08/2013 from 126.4–129.2 m depth are used. All other D4 data from this date are not used in this study.
**Values are mean #breaks/m calculated for each day of analysis. Individual metre-lengths of ice core may have contained more or less breaks.
Melterhead: Three different styles were used: standard = as McConnell et al. (2002); small = smaller cross-sectional area; dual ring = new design with two concentric sample rings available for gas sampling.
Degasser: M=Membrana Liqui-cel Micromodule; IL=IDEX inline degasser.
System response time: Time taken for CH_4 concentration to change between 10 and 90 % of total normalized concentration change resulting from switch between two different air standards mixed with degassed water and circulated through the analytical system (to mirror the pathway of the ice core sample). This value is converted to a depth using the melt rate.

Table S2: Bubble-free layers in Tunu13 ice cores associated with anomalously high CH_4 signals and assumed to be melt layers

Bottom depth (m)	**Thickness (mm)**	**Excess CH_4 (ppb peak height)**	**Continuous or discrete CH_4 anomaly?**	**High CO?**	**Main or B core?**
100.065	10	40	Contin.	Y	B
100.095	<5				
100.135	<5				
100.17	<5				
103.65	<5	15	Contin.	Y	B
103.465	<5				
103.47	<5				
108.855	<5	15	Contin.	Y	Main
112.48	<5	60	Contin.	Y	Main
112.515	5				
113.925	<5	30	Discrete	nd	Main
152.76	<5	40	Contin.	Y	Main
153.29	<5	10	Discrete	N	Main
156.31	<5	25	Discrete	N	Main
180.66	<5	30	Contin.	Y	Main
180.68	<5				
181.75	<5	15	Discrete	nd	Main
194.62	20	20	Discrete	Y	Main
194.625	<5				
201.35	<5	80	Contin.	Y	Main

nd=no data

References

McConnell, J.R., Lamorey, G.W., Lambert, S.W., Taylor, K.C., 2002. Continuous ice-core chemical analyses using inductively coupled plasma mass spectrometry. Environ. Sci. Technol. 36, 7–11. doi:10.1021/es011088z

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