# Excess methane in Greenland ice cores associated with high dust concentrations

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#### Abstract

Ice core records of atmospheric methane  $(CH_4)$  and its isotopic composition provide important information about biogeochemical cycles in the past. Interpreting these data requires that they faithfully record the composition of the atmosphere. In this study, we describe anomalies of up to 30-40 ppb  $CH_4$  that are only observed in dust-rich (>~60 ng Ca/g ice), glacial-period ice measured with standard melt-refreeze methods. The stable isotopic composition of  $CH_4$  is also significantly affected. Results from the GISP2 and NEEM ice cores from Greenland show that excess  $CH_4$  is either released or produced in the presence of liquid water in amounts which are highly correlated with the abundance of  $Ca^{2+}$  and mineral dust in the sample. Additional experiments show that excess  $CH_4$  is unaffected by the addition of  $HgCl_2$  (a microbial inhibitor) and is not related to ice core storage time. Dust concentrations in Antarctic ice cores are an order of magnitude lower than in Greenlandic ice cores and no excess  $CH_4$  was observed in samples from the Antarctic WAIS Divide (WD) and South Pole (SPICE) ice cores. While the overall structure of the ice core atmospheric methane history is minimally impacted by excess  $CH_4$ , the impacts on the isotopic record and on inverse models used to reconstruct  $CH_4$  sources are greater. We propose

Preprint submitted to Geochimica et Cosmochimica Acta

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three potential mechanisms to explain the presence of excess  $CH_4$ : (1) that  $CH_4$  is adsorbed on dust particles prior to deposition on the ice sheet and is slowly desorbed during the melt-extraction step of sample analysis; (2) that dust acts as a micro-environment within the ice sheet for methanogenic extremophiles; or (3) that excess  $CH_4$  is a product of abiotic degradation of organic compounds during the melt-extraction step of sample analysis.

Keywords: Methane, Greenland, Ice Cores, Isotope Geochemistry

# 1 1. Introduction

Ice cores from Greenland and Antarctica preserve the history of atmo-2 spheric methane  $(CH_4)$  and have been used to infer past changes in  $CH_4$ 3 sources (Thompson et al., 1993; Fischer et al., 2008; Bock et al., 2010b; Sowers, 2010; Rosen et al., 2014; Baumgartner et al., 2012, 2014; Rhodes et al., 5 2015; Bock et al., 2017). Natural sources of  $CH_4$  are dominated by microbially 6 produced CH<sub>4</sub> emitted from wetlands largely controlled by temperature and 7 precipitation (Fung et al., 1991; Kirschke et al., 2013; Saunois et al., 2016). 8 The ice core  $CH_4$  record therefore provides important information, albeit 9 indirect, about the history of terrestrial hydroclimate. 10

With traditional sampling techniques it has generally been assumed, with 11 some exceptions, that the polar ice core CH<sub>4</sub> records are not affect by produc-12 tion of  $CH_4$  within the ice (in situ production). Well-documented exceptions 13 include samples altered by the presence of melt layers, which are known to 14 cause elevated levels of  $CH_4$  due to differential dissolution into liquid water 15 (Campen et al., 2003; Mitchell et al., 2013; NEEM Community Members, 16 2013; Rhodes et al., 2016) or the entrainment of  $CH_4$  and nutrient rich sub-17 glacial soils at the ice sheet bed (Souchez et al., 1995; Tung et al., 2005, 2006; 18 NEEM Community Members, 2013). Anomalously high  $[CH_4]$  values were re-19 ported for several samples from the deep GISP2 ice core, but no explanation 20 was provided for a potential cause (Brook et al., 1996). In contrast, elevated 21 concentrations of other species ( $CO_2$ ,  $N_2O$ ,  $CH_3Cl$ ) have been observed by a 22 number of studies (Neftel et al., 1982; Anklin et al., 1995; Smith et al., 1997; 23 Flückiger et al., 1999; Sowers, 2001; Stauffer et al., 2003; Saltzman et al., 24 2009) and linked to in situ processes. 25

Additional anomalies have been observed following the development of a continuous flow analysis technique for measuring ultra-high resolution records of [CH<sub>4</sub>] Stowasser et al. (2012); Rhodes et al. (2013); Chappellaz et al.

(2013). Rhodes et al. (2013) observed infrequent, very brief large spikes in the 29 concentration of  $CH_4$  ([ $CH_4$ ], 20-100 cm depth range, 35-80 ppb magnitude) 30 in the shallow NEEM-2011-S1 ice core which were confirmed by traditional 31 analysis techniques. These spikes were associated with thin layers rich in 32 carbon and nitrogen-containing impurities that may suggest biological in 33 situ processes. Continuous records have also identified a mode of quasi-34 annual variability which affects the preservation of the atmospheric record 35 and create the appearance of abrupt spikes in the record (Rhodes et al., 36 2013, 2015; Mitchell et al., 2015; Fourteau et al., 2017). This variability is 37 related to variations in the depth at which bubbles lose off in the firm layer, 38 which can vary due to seasonal differences in snow properties. At times 30 of changing atmospheric composition these variation in close-off depth can 40 create apparent fast variation in methane concentration that could resemble 41 in situ production. The issue is discussed further below. 42

Here we present several lines of evidence which indicate that the  $[CH_4]$ 43 record preserved in some Greenlandic ice core samples is elevated above the 44 atmospheric concentrations due to a process, different than those described 45 above, which is closely related to the dust content of the samples. In Section 46 2 we discuss evidence from published records of  $[CH_4]$  and show that excess 47  $CH_4$  has also likely affected the isotopic composition of  $CH_4$  in one record. 48 In Section 3 we present  $[CH_4]$  results following successive gas-extraction cy-49 cles which show that  $[CH_4]$  in ice core samples increases during the melt-50 extraction step and allowing us to quantify the amount of  $CH_4$  produced or 51 released<sup>1</sup>. Additional experiments described in Section 3 provide information 52 about the source of excess  $CH_4$ . In Section 4 we discuss potential mechanisms 53 for explaining our results. Lastly, Sections 5 and 6 discuss the implications 54 for interpreting atmospheric  $CH_4$  records from ice cores and the viability of 55 extremophiles in polar ice. 56

<sup>&</sup>lt;sup>1</sup>Here we distinguish release from production, with the latter referring to the chemical or biological reaction resulting in the formation of new  $CH_4$  in the flask during sample analysis while release refers to  $CH_4$  which was already present in the ice sample but was previously in state preventing from exchange into the flask headspace.

# <sup>57</sup> 2. Evidence for excess CH<sub>4</sub> in existing records

#### 58 2.1. Discrepancies between ice core records

 $[CH_4]$  is well sampled over the last glacial cycle from many Greenlandic 59 ice cores (Chappellaz et al., 1993, 2013; Brook et al., 1996, 2000; Dällenbach 60 et al., 2000; Blunier and Brook, 2001; Flückiger et al., 2004; Grachev et al., 61 2007; Baumgartner et al., 2014; Rosen et al., 2014). Dramatic, rapid fluctu-62 ations in atmospheric concentration ( $[CH_4]$ ) are associated with Dansgaard-63 Oeschger events (DO-events) with high concentration associated with north-64 ern hemisphere warm periods (interstadials) and low concentrations during 65 stadial (cold) conditions. These records were typically measured with a melt-66 extraction technique, where discrete samples are melted to liberate the en-67 trapped air providing a single  $[CH_4]$  value for each sample (Chappellaz et al., 68 1993; Flückiger et al., 2002; Blunier et al., 1993; Brook et al., 2000; Mitchell 69 et al., 2011). Specific details of the process vary between laboratories, de-70 tails regarding the technique used at Oregon State University (OSU) are 71 described in Sect. 3 and Appendix B. Measurement uncertainty for indi-72 vidual discrete measurements  $(1-\sigma)$  considered in this manuscript is between 73 5-15 ppb (Baumgartner et al., 2014; Flückiger et al., 2004; Brook et al., 2000). 74 A number of records from Antarctica also exist (EPICA Community 75 Members, 2006; Schilt et al., 2010; Loulergue et al., 2008; Buiron et al., 2012); 76 the most detailed is a continuous flow analysis (CFA) record from the WAIS 77 Divide ice core covering the time period from 9.8 to 67.8 ka (Rhodes et al., 78 2015). CFA involves the gradual melting of long, thin prismatic sticks of the 79 core on a heated funnel-like melt head which produces a stream of water and 80 bubbles for analysis (Stowasser et al., 2012; Rhodes et al., 2013; Chappellaz 81 et al., 2013). Unlike in discrete sampling, the sticks can be stacked to avoid 82 gaps in the record. This continuous technique was also used for the NEEM 83 ice core from North Greenlandic although the NEEM record is only contin-84 uous for  $\sim 30$  cm sections from every 55 cm long melter sample (Stowasser 85 et al., 2012; Chappellaz et al., 2013; Rhodes et al., 2017). 86

Ice cores contain a smoothed record of the local composition of the atmosphere. Due to the fast mixing of air between hemispheres (approximately 1 year) relative to the residence of  $CH_4$  in the atmosphere (8-10 years), changes in the composition of one hemisphere will be quickly transferred to the other hemisphere. Ice cores from Antarctica and Greenland will record these changes as simultaneous events of unequal magnitudes. This is confirmed by comparing the NEEM continuous record with the WAIS Divide <sup>94</sup> continuous record (Fig. 1c). Although the values of  $[CH_4]$  are observed to <sup>95</sup> be higher in the NEEM continuous record due to the uneven geographic dis-<sup>96</sup> tribution of CH<sub>4</sub> sources, changes in concentration essentially synchronous <sup>97</sup> between the hemispheres (Rhodes et al., 2017).

By comparing  $[CH_4]$  records we identify variations which are observed 98 in one ice core but lack an analogue in the continuous records from the 99 NEEM and WAIS Divide ice cores (Fig. 1, see Fig. A.1 for comparison of 100 [CH<sub>4</sub>] records on the gas age scale). In this figure the WAIS Divide record is 101 chosen as a reference because it is independently calibrated and because few 102 gaps exist in the data. As noted by Rhodes et al. (2017), centennial-scale 103 variability is well replicated in the WAIS Divide and NEEM continuous data 104 sets and lends to the credibility of the NEEM record (Fig. 1c). To aide visual 105 comparison, the WAIS Divide  $[CH_4]$  record has been shifted in Fig. 1. While 106 the NEEM continuous  $[CH_4]$  record would allow for a more direct comparison 107 to discrete Greenlandic records, doing so would be circular because it was 108 calibrated to the discrete  $[CH_4]$  records in a piecewise manner (Chappellaz 109 et al., 2013). 110

The comparison of discrete records with the continuous records shows spe-111 cific intervals of elevated methane concentrations in the discrete data sets. 112 These discrepancies are especially visible in the NGRIP [CH<sub>4</sub>] record  $\sim 500$ 113 years prior to the onset of Dansgaard-Oeschger event-8 and 12 (39.5-40.0 ka 114 and 48.0-48.5 ka, hatched boxes in Fig. 1). In both of these time periods 115 concentrations in the NGRIP  $[CH_4]$  record increased by ~30 ppb during no-116 tably stable periods in the continuous NEEM or WAIS Divide  $[CH_4]$  records 117 (Chappellaz et al., 2013; Rhodes et al., 2015). These discrepancies are much 118 larger than the 5.9 ppb measurement error of the NGRIP ice core (Baum-119 gartner et al., 2014). Since samples for the NGRIP ice core were measured 120 in random order and these periods consist of ten and seven measurements, 121 respectively, these offsets are not likely to be related to instrumental arti-122 facts. There are similar features in the GISP2 and GRIP records (Fig. 1b, 123 c), although the chronological uncertainties and sample resolution of these 124 records limit precise comparison to the NEEM and WAIS Divide records. 125

Other notable differences are observed during DO-10 and 11 (40.95-41.35 ka and 42.68-43.25 ka, respectively) and are again clearest in the NGRIP [CH<sub>4</sub>] record (Fig. 1a). During DO-10, peaks at the onset and at the termination of the interstadial are observed in both the NEEM and WAIS Divide [CH<sub>4</sub>] records with similar values at both peaks and a near constant offset between the records (Fig. 1c). In contrast, [CH<sub>4</sub>] observed in the NGRIP <sup>132</sup> ice core tends to increase throughout the interstadial resulting in  $[CH_4]$  at <sup>133</sup> the end of the interstadial being ~40 ppb ( $\pm 8.4$  ppb) higher than at the <sup>134</sup> beginning. A similar feature is observed during DO-11 when comparing the <sup>135</sup> NGRIP and WAIS Divide records, however it is not possible to verify this <sup>136</sup> feature because of a gap in the NEEM record at this time.

Elevated [CH<sub>4</sub>] in normal ice was occasionally observed in previous stud-137 ies, such as in the GISP2 record at 37.87 ka, 38.33 ka, and 47.27 ka (Brook 138 et al., 1996) and in the shallow NEEM-2011-S1 ice core (Rhodes et al., 2013). 139 With the recent ultra-high resolution  $[CH_4]$  records inconsistencies between 140 ice cores are more clearly discerned. In general, we observe that in certain 141 sections Greenlandic ice samples measured with a discrete wet extraction 142 technique appear to be elevated in comparison to the records measured with 143 a continuous technique. These elevated sections are much more extensive 144 than the in situ-derived spikes observed in Rhodes et al. (2013) and have not 145 counterparts in the continuous WAIS Divide or NEEM records. This implies 146 that additional  $CH_4$  is related to the measurement technique, as discussed 147 in detail below. Although in both cases the sample is melted, with CFA the 148 gas is quickly separated from the liquid stream (2-3 minutes) providing only 149 a short time period for the release or production of  $CH_4$  in comparison to 150 discrete measurements (typically 15-30 minutes). Additionally the discrete 151 method usually, but not always, involves refreezing the sample after gas ex-152 traction which could influence how much  $CH_4$  remains trapped in the sample 153 water/ice. 154

### $_{155}$ 2.2. Links between proxies of dust and excess $CH_4$

Discrete  $[CH_4]$  measurements from Greenlandic ice samples tend to be 156 elevated relative to the continuous records when the ice age of the sample 157 corresponds to a stadial period when  $Ca^{2+}$  concentrations are high (grav 158 bars in Fig. 1).  $Ca^{2+}$  is commonly assumed to be a proxy for continental 159 dust (Steffensen, 1997) but covaries with the concentration of many other 160 impurities (Mayewski et al., 1997; Schüpbach et al., 2018). Variations in its 161 abundance are recorded in ice cores throughout Greenland. The ice cores con-162 sidered here have similar concentrations of  $Ca^{2+}$  (Rasmussen et al., 2014). 163 Air in an ice core sample is offset in depth from ice of the same age be-164 cause bubble close off only happens at a depth of 50-100 m within the firm 165 (Schwander and Stauffer, 1984). To account for this offset we have translated 166 the  $[CH_4]$  measurements on to the GICC05 ice age scale (Rasmussen et al., 167

<sup>168</sup> 2014) to allow direct comparison to variations of  $Ca^{2+}$  (Fig. 1e, Rasmussen <sup>169</sup> et al. 2014).

As shown in hatched boxes in Fig. 1, a 30 ppb increase in  $[CH_4]$  is ob-170 served prior to both DO-8 and DO-12 in the NGRIP  $[CH_4]$  record at the same 171 depth where  $Ca^{2+}$  increases from ~60 ng/g to >600 ng/g. Concentrations 172 of  $CH_4$  remain elevated as long as  $Ca^{2+}$  concentrations are high and then 173 decrease by 10-20 ppb when  $Ca^{2+}$  returns to interstadial values at 38 and 47 174 ka (ice age). Several samples with elevated  $[CH_4]$  values were also observed 175 in the GISP2 and GRIP records prior to DO-8 and DO-12 (as expressed in 176  $[CH_4]$ ) and correspond to dust-rich ice in those ice cores (Fig. 1b, d). The 177 link between  $Ca^{2+}$  and elevated  $[CH_4]$  is also evident as a small minimum in 178 both the NGRIP and GISP2 [CH<sub>4</sub>] records during DO-9 ( $\sim$ 40 ka ice age), a 179 brief period of low dust concentration between two stadials. Elevated values 180 may also exist during other dusty periods but the identification is compli-181 cated by the coincidence of abrupt changes of both  $[CH_4]$  and  $Ca^{2+}$  (such as 182 at 35.5 and 36.5 ka ice age), by age uncertainties of the  $[CH_4]$  records (such 183 as at 40-41 ka), or because the low-resolution of older records resulted in no 184 stadial ice being measured for  $[CH_4]$  (as is the case for the GISP2 and GRIP 185 ice cores at 44.6 and 49.3 ka). 186

#### 187 2.3. Isotope anomalies associated with excess $CH_4$

Atmospheric CH<sub>4</sub> is isotopically heavier (higher isotopic ratios of  ${}^{13}C/{}^{12}C$ 188 and  ${}^{2}H/{}^{1}H$ ) than the globally integrated CH<sub>4</sub> source due to isotope fraction-189 ation in atmospheric sink reactions. This is particularly true of  $\delta D(CH_4)$ , for 190 which the atmosphere is heavier than all significant sources and the isotopic 191 difference of the atmosphere from the globally integrated source composition 192 is  $\sim 200\%$  (Quay et al., 1999; Whiticar and Schaefer, 2007). For this rea-193 son, it is likely that any contribution from excess  $CH_4$ , which would not be 194 subject to atmospheric sink processes, will significantly lower the measured 195 isotopic value. 196

 $\delta D(CH_4)$  has been measured for the time period 33.68-40.99 ka gas-age 197 (34.9-41.9 ka ice-age) from samples from the NGRIP ice core (Bock et al., 198 2010b) using a wet extraction technique (Bock et al., 2010a). Unlike the melt-190 refreeze techniques used to measure  $[CH_4]$ , the technique used by Bock et al. 200 (2010a,b) does not involve refreezing the sample. Figure 2 shows records of 201  $[CH_4]$  and  $\delta D(CH_4)$  plotted on the NGRIP GICC05 ice age scale for direct 202 comparison to the NGRIP  $Ca^{2+}$  record (Rasmussen et al., 2014). Several 203 large negative isotopic excursions were observed that were difficult to explain 204

because of the lack of a correspondingly large change in concentration or a 205 mechanism which would cause a switching between different source types. 206 The largest feature is a 16% depletion which begins at 39.74 ka (2106 m, 207 40.0 ka ice-age),  $\sim 500$  years prior to the onset of DO-8 as observed in the 208  $[CH_4]$  record (Fig. 2b) and is co-registered in depth with a >10x increase 209 in  $Ca^{2+}$  and the late-stadial rise of 30 ppb in  $[CH_4]$  discussed in Sect. 2.1. 210 Two other well sampled excursions, both depletions of >6% (35.3-36.6 ka 211 and 40.4-41.1 ka), are also associated with dust peaks. The one other well 212 sampled excursion noted by Bock et al. (2010b) (2048-2069 m, 36.5-37.0 ka 213 gas-age, 37.5-38.1 ka ice-age) is not associated with high dust concentrations 214 but is also not associated with significant variability of  $[CH_4]$ . Since these 215 samples were not refrozen prior to the gas extraction step, evidence of excess 216  $CH_4$  in this record implies that its release/production is not related to the 217 refreezing of the sample. 218

Ice samples from the GISP2 ice core were also measured for  $\delta D(CH_4)$ 219 using a wet extraction technique (Sowers, 2006). A seven-sample subset of 220 these overlaps in age with the  $\delta D(CH_4)$  measurements from NGRIP. This 221 subset reveals a  $\sim 16\%$  depletion concurrent with the abrupt increase in 222  $[CH_4]$  during the onset of DO-8. Although the magnitude of this depletion is 223 similar to the one seen in the NGRIP ice core, the depletions differ in their 224 phasing with respect to changes in  $[CH_4]$  and the depletion in the GISP2 ice 225 core is not associated with an increase in dust concentration. The GISP2 226  $\delta D(CH_4)$  record is difficult to interpret: first, because it only encompasses a 227 brief time period (39.05 to 39.60 ka, ice age) during which  $[CH_4]$  increased 228 abruptly; second, because there is a large offset between the GISP2 and 229 NGRIP  $\delta D(CH_4)$  records (Umezawa et al., 2018); and, third, because the 230 GISP2 record exhibited large sample-to-sample variability during the more 231 detailed deglacial section (Sowers, 2006). 232

# $_{233}$ 3. Experimental investigation of excess $CH_4$

# 3.1. Measurement of release/production of $CH_4$ in the OSU analytical system Excess $CH_4$ was measured at Oregon State University (OSU) with a multiple refreeze process. First, $[CH_4]$ was measured following the typical procedure described by Grachev et al. (2009) and Mitchell et al. (2013) with updates described in Lee et al. (2018). Briefly, 32-65 g ice samples are placed in glass flasks which are then attached to a high vacuum line. Flasks are

 $_{240}$  immersed in a chilled ethanol bath set to  $-70^{\circ}$  C to keep the samples frozen.

After laboratory air has been evacuated, the flasks are sealed from the vac-241 uum and the samples are melted in a hot water bath, initially 50° C ( $\pm 1^{\circ}$ 242 C), for 30 minutes to liberate the air into the flask headspace. Samples 243 typically require 15-25 minutes to finish melting, depending on the size of 244 samples and whether the ice is bubbly or clathrated. The flasks are then 245 re-immersed in the cold ethanol bath. Once the melt water is completely 246 refrozen, air from the headspace is expanded into a sample loop in a gas 247 chromatograph (GC). Pressure in the sample loop is recorded and the air is 248 injected into the GC system for  $[CH_4]$  measurement. Expansion air in the 240 flask headspace into the GC system is repeated four times for four individual 250 readings during this measurement set. Absolute uncertainty of  $[CH_4]$  values 251 for measurements presented here is 1.8 ppb (pooled standard deviation of 252 depths sampled multiple times, n=96 sample depths). 253

Following the typical procedure we begin additional analysis to quantify 254 excess  $CH_4$ . The refrozen ice is left in the glass vessels with the remaining 255 sample air (about 30%) after the GC measurement. The melt-refreeze ex-256 traction step is repeated and then we re-measure the  $[CH_4]$  by expanding air 257 in the headspace into the GC either 2 or 4 times. The difference between the 258 average of the first and second set of measurements is referred to as  $\Delta CH_4$ . 259 Uncertainty of  $\Delta CH_4$  was determined to be 4.4 ppb (pooled standard de-260 viation of replicated sample depths). Interpretation of  $\Delta CH_4$  is discussed 261 below. 262

This procedure was applied to ice samples from several ice cores with very 263 different impurity compositions and concentrations (data available https: 264 //www.ncdc.noaa.gov/paleo/study/27610). Most of our samples are from 265 the Greenlandic GISP2 ice core (154 samples) and the Antarctic WAIS Divide 266 ice core (82 samples). We also include measurements from the NEEM ice core 267 from Greenland (40 samples) and the Antarctic South Pole ice core (SPICE 268 ice core, 19 samples) as well as measurements made on bubble free ice (BFI, 269 62 samples) that we produce using ultra-pure deionized water and which 270 we interspersed with our other samples. Temporally, our samples include 271 overlapping measurements from the WAIS Divide, GISP2, and NEEM ice 272 cores dated between 42 - 50 ka and five more samples from the GISP2 ice 273 core from 72-75 ka (Sect. 3.4). Samples from the SPICE ice core are from 274 various ages during the last glacial cycle. 275

Figures 3a, b and 4a, b show results from the first and second set of [CH<sub>4</sub>] measurements and of  $\Delta$ CH<sub>4</sub> for samples from the GISP2 and NEEM ice cores.  $\Delta$ CH<sub>4</sub> is observed to be positive for almost every sample, including

BFI samples. Small increases in  $[CH_4]$  are expected due the higher solubility 279 of  $CH_4$  in comparison to  $N_2$  and  $O_2$  (the main components of air). This 280 causes the melt water to be slightly enriched in  $CH_4$  with respect air in the 281 headspace. The refreezing process does not perfectly expel all gases from 282 the melt-water. During the second melt-extraction step, this  $CH_4$  degases 283 from the melt-water due to the reduced gas pressure from GC measurements 284 and causes  $[CH_4]$  in the headspace to increase. The quick refreezing of the 285 ice sample is one way which the OSU measurement methodology varies from 286 other laboratories (Chappellaz et al., 1997; Flückiger et al., 2004). The trap-287 ping of gas in the refrozen sample is referred to as the solubility effect and 288 can explain  $\Delta CH_4$  values observed for samples with low-dust concentrations. 289 For GISP2 and NEEM samples,  $\Delta CH_4$  closely follows the quantity of 290  $Ca^{2+}$  in the sample (Fig. 3d and 4d). Although solubility of gases decrease 291 with increasing concentration of ions, the large values of  $\Delta CH_4$  in samples 292 with high concentrations of  $Ca^{2+}$  exceeds what is possible by solubility effects 293 alone (i.e. more  $CH_4$  is degassed than could be trapped in the ice). To 294 quantify the amount of additional  $CH_4$  (excess  $CH_4$ ) the effects of solubility 295 must be removed. Another important observation is that our approach is 296 only feasible because the release/production of excess  $CH_4$  is slow relative 297 to the melt phase of extraction, i.e. the release/production of excess  $CH_4$ 298 is not complete during the first extraction and resumes during sequential 299 melt-extractions. This implies that  $\Delta CH_4$  is sensitive to the duration of the 300 melt-refreeze extraction and necessitates consistent extraction conditions. 301

### 302 3.2. Quantifying excess CH<sub>4</sub> from measurements

To quantify the total amount of excess  $CH_4$  generated we need to con-303 strain the quantity that remains in the refrozen meltwater at the end of the 304 second melt-refreeze step. This cannot be directly measured. Instead we 305 estimate this value by determining the typical solubility effect for each ice 306 core empirically based on samples with low-dust content and accounting for 307 variations in  $[CH_4]$ , total air content, sample mass, and for differences in the 308 volume between sample flasks (Description of the methods used to determine 309 solubility effects are provided in Appendix B). This allows us to estimate an 310 expected  $\Delta CH_4$  for each sample. Excess  $CH_4$  is then defined as difference 311 between the measured  $\Delta CH_4$  and the expected value and is provided in units 312 of moles of  $CH_4$ . The equations used to quantify the amount of excess  $CH_4$ 313 released/produced  $(n_{xs}^*)$  are provided in Appendix C. 314

Figures 3c and 4c show  $n_{xs}^*$  versus depth for the GISP2 and NEEM ice 315 cores, respectively. Values of  $n_{xs}^*$  range from 0 to  ${\sim}6$  picomoles and are 316 closely related to the measured value  $\Delta CH_4$ . Pooled standard deviation of 317 replicate measurements of  $n_{xs}^*$  is 0.4 picomoles and is independent of  $n_{xs}^*$  and 318 from which core it was determined. Values of  $n_{xs}^*$  from the WAIS Divide 319 or SPICE ice core samples were not statistically different than 0. Those 320 results were not plotted but are included in the Supplementary Material. 321 The largest value of  $n_{xs}^*$  was observed in a dusty sample from the NEEM ice 322 core (Fig. 4c) and would have been equivalent to a 9% (40 ppb) increase in 323  $[CH_4]$  if released/produced during the first melt extraction. Although some 324 differences exist, the  $\sim 30-40$  ppb impact of excess CH<sub>4</sub> on GISP2 and NEEM 325  $[CH_4]$  measurements preceding DO-12 is similar to that inferred for the GRIP 326 and NGRIP  $[CH_4]$  record for the same time period (Sect. 2.1). Since both 327 the GRIP and NGRIP  $[CH_4]$  measurements were made with a similar melt-328 extraction technique to that used at OSU (Chappellaz et al., 1997; Blunier 329 et al., 1998; Flückiger et al., 2002; Baumgartner et al., 2014), these records 330 are also likely affected by excess CH<sub>4</sub>. 331

In both the GISP2 and NEEM ice core results,  $n_{xs}^*$  is highly correlated 332 with the concentration of chemical impurities (Fig. 5, Table 1). Elements 333 commonly associated with continental dust (Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>) show the 334 highest correlation to the GISP2 results ( $R^2=0.78$  with  $Ca^{2+}$ , n=108 samples) 335 while ammonium and nitrate (common nutrients) have a significantly weaker 336 correlation ( $R^2=0.20$  and  $R^2=0.33$ , respectively). Strong relationships are 337 also observed between the NEEM  $n_{xs}^*$  measurements with both Ca<sup>2+</sup> and 338 particle counts from the NEEM ice core ( $R^2=0.64$  and  $R^2=0.59$ , respectively, 339 n=32 samples). 340

A regression between  $Ca^{2+}$  concentration and  $n_{xs}^{*}$  for the GISP2 results 341 indicates that  $\sim 5 \pm 0.5 \ \mu \text{mol}$  of CH<sub>4</sub> (95% CI) are produced per mole of 342  $Ca^{2+}$  in the sample (150 ng  $CH_4/g$   $Ca^{2+}$ , Fig 5). We emphasize that this is 343 simply the observed statistical association and it does not imply a stoichio-344 metric relationship. Since the process which releases/produces excess  $CH_4$  is 345 not allowed to continue to completion and different laboratories melt their 346 samples at different temperatures and for different lengths of time, this ratio 347 is probably specific to the OSU system and measurement procedure. Re-348 gardless, we find that the relationship is consistent for GISP2 samples from 349 both the 42-50 ka period as well as the 5 samples from 72-75 ka (Fig. 5). We 350 attribute the lack of excess CH<sub>4</sub> in WAIS Divide and SPICE ice core samples 351 to the much lower dust concentrations (typically an order of magnitude less) 352

<sup>353</sup> and possibly to differences in dust mineralogy.

An ad hoc correction to the measured concentration can be made by sub-354 tracting  $n_{xs}^*$  from the first set of measurements (which followed the first melt-355 extraction). While  $n_{xs}^*$  represents the quantity of CH<sub>4</sub> released/produced 356 during the second extraction, differences in melting conditions between the 357 first and second extractions make it difficult to assess whether this is an 358 overestimate or underestimate of  $CH_4$  released/produced during the first ex-359 traction. For simplicity we assume an equal addition of  $CH_4$  during each of 360 these steps. 361

In Fig. 6, corrected  $[CH_4]$  records from the GISP2 and NEEM ice cores 362 are plotted with the WAIS Divide and NEEM continuous records. The 30 ppb 363 pre-DO-12 increase in  $[CH_4]$ , well captured in the uncorrected measurements, 364 is not present in the corrected GISP2 record. Better agreement in absolute 365 concentrations between the NEEM discrete measurements and GISP2 mea-366 surements is observed after the correction. Agreement of multi-decadal to 367 multi-centennial scale variability, particularly during DO-12, is also observed 368 between the corrected records of the NEEM and GISP2 ice cores and the 369 WAIS Divide and NEEM continuous records but not in the uncorrected dis-370 crete records. While these observations lead us to believe that our ad hoc 371 correction has improved our interpretation of atmospheric  $[CH_4]$ , more work 372 is needed to develop a quantitative and more precise correction for  $[CH_4]$ 373 measurements. Such a correction will need to be verified by measurements 374 of  $[CH_4]$  unaffected by excess  $CH_4$  from dusty Greenlandic ice samples. 375

#### 376 3.3. An estimate of the $\delta D(CH_4)$ signature of excess $CH_4$

The effect of excess  $CH_4$  on  $\delta D(CH_4)$  can be assessed using the NGRIP [CH<sub>4</sub>] (Baumgartner et al., 2014) and  $\delta D(CH_4)$  records (Bock et al., 2010b). Both records were measured with a melt-extraction technique (Bock et al., 2010a; Flückiger et al., 2004; Baumgartner et al., 2014). Here, we assume that the ice core sample represents a two-component mixture with end members of atmospheric air and excess  $CH_4$  (represented by Eqn. 1).

$$\delta D(CH_4)_{model} = (1 - f_{xs}) \cdot \delta D(CH_4)_{atm} + f_{xs} \cdot \delta D(CH_4)_{xs}$$
(1)

In this model, the measured stable isotopic composition of  $CH_4$  is dependent on the isotopic compositions of the atmospheric component ( $\delta D(CH_4)_{atm}$ ), the excess component ( $\delta D(CH_4)_{xs}$ ), and the relative contribution of excess  $CH_4$  ( $f_{xs} = [CH_4]_{xs}/[CH_4]_{measured}$ ). In both the NEEM and WAIS Divide continuous  $[CH_4]$  records, stable [CH<sub>4</sub>] was observed for the ~1000 year period preceding DO-8 (Chappellaz et al., 2013; Rhodes et al., 2015). We use this time period to estimate  $[CH_4]_{xs}$ , assuming that atmospheric  $[CH_4]$  was constant and comparing the difference of the NGRIP  $[CH_4]$  and the atmospheric value to the concentration of Ca<sup>+2</sup>. The resulting relationship of Ca<sup>2+</sup> is:  $[CH_4]_{xs}$  (ppb) =0.091·(Ca<sup>2+</sup> (ng/g) -43). Equation 1 can then be rearranged:

$$\delta \mathcal{D}(\mathcal{CH}_4)_{model} = \delta \mathcal{D}(\mathcal{CH}_4)_{atm} + (\delta \mathcal{D}(\mathcal{CH}_4)_{xs} - \delta \mathcal{D}(\mathcal{CH}_4)_{atm}) \cdot \frac{0.091 \cdot (\mathcal{Ca}^{2+} - 43)}{[\mathcal{CH}_4]_{measured}}$$
(2)

We solve for  $\delta D(CH_4)_{xs}$  using a best-fit two-sided regression comparing 394  $\delta D(CH_4)_{model}$  to the NGRIP  $\delta D(CH_4)$  record ( $\delta D(CH_4)_{measured}$ ) following 395 the method of York et al. (2004) which accounts for errors in both variables. 396 Weights for the fit are derived from measurement uncertainties of  $[CH_4]$ , Ca<sup>2+</sup> 397 (constant 10%), and  $\delta D(CH_4)_{measured}$  (constant 3.4‰) and the regression 398 uncertainty between  $[CH_4]$  and  $Ca^{2+}$ . Best fit values were determined to 399 be  $\delta D(CH_4)_{xs}$  = -293‰ (± 31‰ 95% CI, n=51, R<sup>2</sup> = .53) and  $\delta D(CH_4)_{atm}$  = -400 82.2% (± 0.7% 95% CI). This provides a good fit to the NGRIP  $\delta D(CH_4)$ 401 record despite the assumption of a constant atmospheric history (Fig. 7). 402

#### 403 3.4. Microbial inhibition experiment

As described in sections 3.1-3.3, our observations indicate that a pre-404 viously unknown process either releases or produces  $CH_4$  during the melt-405 refreeze extraction step of analysis. One possibility is that microbial pro-406 duction occurs when the sample is melted. Microbial methanogenesis favors 407 anoxic conditions ( $[O_2] < 0.5 \text{ mg} \cdot \text{L}^{-1}$ ), a condition which is met during melt-408 ing of our samples because of the small amount of air remaining in the sample 409 flask after evacuating contemporary air. Under this hypothesis, production 410 of  $CH_4$  would scale with either the nutrient availability, cell abundance, or 411 both. 412

We tested this possibility by inhibiting biologic activity with 25  $\mu$ L of saturated mercuric chloride (HgCl<sub>2</sub>) solution added to selected samples (54-58 g). This quantity of HgCl<sub>2</sub> is enough to inhibit microbial activity in samples of sea water of similar volume (Oxtoby et al., 2016). A control of each sample was also measured without HgCl<sub>2</sub>. Samples used in this test were from the GISP2 ice core and date between 72-75 ka which includes DO-20, a period of low dust concentrations ( $[Ca^{2+}]<35 \text{ ng}\cdot\text{g}^{-1}$ ), and the succeeding dusty stadial interval ( $[Ca^{2+}]>350 \text{ ng}\cdot\text{g}^{-1}$ ). These GISP2 samples were previously measured by Grachev et al. (2009) on an earlier version of the OSU system.

Figure 8 shows the results of this test. Despite the  $\sim 10$  years between 423 when these samples were measured, our new measurements reproduce values 424 from Grachev et al. (2009) well within measurement uncertainty (mean dif-425 ference of 3.6 ppb  $\pm$  1.4 ppb, measurement uncertainty from Grachev et al. 426 (2009) of 2 ppb, absolute uncertainty of new measurements of 2.4 ppb). 427 There was no difference in  $[CH_4]$  between samples that had been poisoned 428 with  $HgCl_2$  and their replicate which had not, in either the first or second 429 set of measured concentrations (Fig 8). The ratio of  $n_{xs}^*$  compared to the 430 number of moles of  $Ca^{2+}$  in the samples was consistent with that observed 431 in Sect. 3.2. This set of observations indicates that either microbes were 432 tolerant of this concentration of  $HgCl_2$ , which seems unlikely, that  $CH_4$  is 433 produced abiotically, or that  $CH_4$  was formed prior to the original analysis 434 of the ice samples and released during sample processing. 435

#### $_{436}$ 4. Potential sources and pathways for excess $CH_4$

In section 2 and 3 we provide evidence for excess  $CH_4$  and attempt to quantify the effect of excess  $CH_4$  in ice core samples measured at OSU. To summarize our observations of excess  $CH_4$  in Greenlandic ice core samples:

- Release/production of excess CH<sub>4</sub> occurs slowly (hours) when liquid
  water is present during the melt-extraction of air from the ice sample
  (Sect. 3.1 and 3.2). Excess CH<sub>4</sub> is observed whether or not the sample
  is refrozen after extraction.
- Elevated CH<sub>4</sub> values are not observed in measurements using a continuous technique which separates gases from the melted sample within minutes. This distinguishes excess CH<sub>4</sub> from the spikes observed by Rhodes et al. (2013).
- Release/production of excess CH<sub>4</sub> is not inhibited by the addition of HgCl<sub>2</sub> to the sample (Sect. 3.4).
- The amount of excess  $CH_4$  released/produced during extraction is correlated with the amount of dust in the ice core sample (Sect. 2.2 and

452 3.2) and the relationship is the same for samples dated between  $\sim$ 42-50 ka and  $\sim$ 72-75 ka (Sect. 3.4).

- The amount of excess CH<sub>4</sub> released/produced is independent of the length of time the ice core has been stored since it was recovered (Sect. 3.4).
- Excess CH<sub>4</sub> was measured in samples from multiple Greenlandic ice cores (GISP2 and NEEM ice cores), but not in Antarctic ice core samples (WAIS Divide and SPICE) using the standard extraction time (Sect. 3.1 and 3.2). Analogous anomalies in [CH<sub>4</sub>] can be observed in the GRIP and NGRIP records (Blunier et al., 1998; Baumgartner et al., 2014) (Sect. 2.1).
- $\delta D(CH_4)_{xs}$  is estimated to be ~-293‰ (± 31‰ 95% CI), which consistent with biogenically produced CH<sub>4</sub> (Sect. 3.3).

We now review several possible mechanisms which could lead to the addition of excess  $CH_4$ , and evaluate their viability.

# 467 4.1. Artifacts of drilling and storage

Artifacts may include any production or addition of CH<sub>4</sub> during or after 468 the drilling of the ice core. This may include direct contamination, such as 469 the closing of bubbles or cracks in the ice core after extraction from the ice 470 sheet (Aydin et al., 2010) which can trap modern air with high  $[CH_4]$  or 471 contaminate the sample with drill fluid. As is the case with many types of 472 artifacts, post-coring bubble or fracture close-off would not produce/release 473 CH<sub>4</sub> during the second melt-refreeze extraction and therefore would not pro-474 duce an excess signature as we have defined it. Additionally, it is unlikely 475 that this sort of direct contamination would only affect records from Green-476 land and result in a close correlation with the dust content of the sample. We 477 therefore find it unlikely that excess  $CH_4$  is related to a direct contamination 478 of the ice core. 479

Artifacts could also include indirect contamination, for example an unknown reaction involving drill fluid or the introduction of microbes to the ice core after the core was recovered. We do not expect that these processes are the cause of our measured excess CH<sub>4</sub> as samples are trimmed thoroughly so that any such contaminant is removed. Additionally, if post-coring production happens it must occur during the first few years after drilling based

on: (1) the good agreement between our measured  $[CH_4]$  values from GISP2 486 with older measurements (Grachev et al., 2009) and (2) the similar relation-487 ship between excess  $CH_4$  and  $Ca^{2+}$  observed for the GISP2 ice core drilled 488 in 1993 and the NEEM ice core which was drilled in 2011. All samples were 489 measured between July 2016 and February 2017. Given the storage condi-490 tions (typically -30 to  $-50^{\circ}$  C) it seems unlikely that microbes could produce 491 the observed excess  $CH_4$  in the short time frame and that production would 492 stop. 493

#### 494 4.2. "In Vitro" production of $CH_4$

<sup>495</sup> A special case of an artifact is the production of  $CH_4$  under the specific <sup>496</sup> conditions of the measurement procedure. We refer to the possibility of <sup>497</sup> biologic or chemical production of  $CH_4$  during the melt-extraction process <sup>498</sup> as "in vitro" (in reference to the glass flasks used for  $CH_4$  analysis). In <sup>499</sup> vitro production matches many of the observations of excess  $CH_4$  such as the <sup>500</sup> production would occur in the presence of water, would be time dependent, <sup>501</sup> and would potentially be nutrient or cell limited.

We believe microbial production in the flask is unlikely given that the 502 addition of excess  $CH_4$  was unhindered in the presence of  $HgCl_2$  (Sect. 3.4) 503 and that the negative  $\delta D(H_2O)$  (typical values between -300 to -320‰, Jouzel 504 et al. 2007) would likely result in an isotopically lighter signature than in-505 ferred for  $\delta D(CH_4)_{xs}$  (Sect. 3.3). CH<sub>4</sub> can also be produced abiotically from 506 organic carbon (Wang et al., 2017; Hurkuck et al., 2012), a pathway which 507 would not be affected by HgCl<sub>2</sub>. These mechanisms include UV irradiation 508 (Fraser et al., 2015), heating (Jugold et al., 2012; Hurkuck et al., 2012), or 509 the presence of reactive oxidating species to cleave organic molecules (Ju-510 gold et al., 2012). All of these studies involved soil samples and mechanisms 511 that would require large quantities of organic carbon precursor. While simi-512 lar conditions are not present during our experiments we cannot definitively 513 rule out an abiotic mechanism. 514

#### 515 4.3. Production related to surface melt events

<sup>516</sup> Spikes in [CH<sub>4</sub>] in ice cores have been found in the presence of refrozen <sup>517</sup> surface melt layers (Campen et al., 2003; Mitchell et al., 2013; NEEM Com-<sup>518</sup> munity Members, 2013; Rhodes et al., 2016). These spikes can partially be <sup>519</sup> explained by the higher solubility of CH<sub>4</sub> than the major air constituents. <sup>520</sup> However, in some cases the measured [CH<sub>4</sub>] exceeded what was expected from <sup>521</sup> equilibrium solubility alone suggesting that surface melt promotes some other

in situ process which further enhances  $[CH_4]$  (Campen et al., 2003; NEEM 522 Community Members, 2013; Schmitt et al., 2014; Rhodes et al., 2016). We 523 do not believe that the elevated  $[CH_4]$  that we observe in the NEEM and 524 GISP2 ice cores are related to the occurrence of melt layers for two reasons. 525 First, the elevated  $[CH_4]$  values we measured occur only in ice that was de-526 posited during cold stadial periods but not during warm interstadials when 527 melt layers may be more frequent. Second, the mechanism would not ex-528 plain the continued addition of CH<sub>4</sub> in sequential melt-refreeze cycles during 529 sample processing. 530

However, production due to melt layer formation is similar to the process 531 which releases/produces excess  $CH_4$  described here in that the increase in 532  $[CH_4]$  appears to be related to the presence of liquid water, implying that 533 the unknown process affecting melt layers could be similar to that affecting 534 discretely measured samples. Interestingly, Campen et al. (2003) measured 535 anomalies in  $[CH_4]$  with a dry extraction technique and the possibility of 536 melt layers affecting these samples was excluded by measurements of noble 537 gas ratios on co-registered depths. Without the presence of water during 538 extraction the elevated values they observed were probably the result of a 539 different process than that observed here. 540

#### 541 4.4. Annual "trapping" signal

Mitchell et al. (2015) and Rhodes et al. (2013, 2016) observed a quasi-542 annual variability of  $[CH_4]$  preserved in multiple ice cores which is related to 543 seasonal differences in ice density. Fourteau et al. (2017) showed that these 544 variations can also be observed in ice during the last glacial period. These 545 seasonal layers seal off bubbles at different depths, thus preserving air alter-546 nating between older and younger ages. Given a period of rapidly changing 547  $[CH_4]$ , slow firm densification rates, and strong layering, the magnitude of the 548 annual signal was found to be up to 40 ppb. Although the 40 ppb trapping 549 signal is of similar magnitude as the estimated impact of excess  $CH_4$  that we 550 measured, it would not produce a continuing increase of  $[CH_4]$  over multiple 551 melt-extraction cycles. 552

#### 553 4.5. In Situ production of $CH_4$

The interiors of polar ice sheets are harsh environments for life due to the extreme cold, the limited liquid water, and the scarcity of nutrients. However, two micro-environments within ice sheets which may be suitable for life have been proposed; at triple-junctions between ice grains and on the <sup>558</sup> surface of dust particles, such as clays, where pressure or ion concentration <sup>559</sup> prevents water from freezing and nutrients may be concentrated (Price, 2000; <sup>560</sup> Tung et al., 2005; Price, 2007). In situ production fits many of our observa-<sup>561</sup> tions about excess  $CH_4$ , but only if the produced  $CH_4$  would be adsorbed or <sup>562</sup> trapped at the production site, e.g. onto particles.

In situ production of  $CH_4$  would cause increased  $[CH_4]$  with depth (time) 563 until either nutrients are exhausted or conditions (pressure, temperature) no 564 longer support production. Time-dependent production would be observed 565 as changes in the ratio of  $n_{xs}^*$  compared to the number of moles of Ca<sup>2+</sup>. 566 However, this relationship is remarkably consistent across the  $\sim 30$  ka time 567 period covered by our GISP2 samples. This would imply that in the GISP2 568 ice core the production of  $CH_4$  has ceased to occur at a significant rate in ice 569 that is of at least 42,000 years old, the age of our youngest sample (2300 m). 570 Measurement of shallower (younger) samples will be required to conclude 571 whether in situ production exists in younger ice. 572

Microbial methane production is generally inhibited by the presence of 573 oxygen. The partial pressure of oxygen in bubbles in the ice sheet is elevated 574 above ambient levels due to the weight of overlying ice. The high oxygen 575 pressures would likely prevent in situ microbial production. As was the case 576 with the hypotheses of post-coring microbial production or in vitro produc-577 tion, if in situ microbial production of  $CH_4$  did occur, it would be expected 578 to have an isotopic composition lower than the estimated  $\delta D(CH_4)_{xs}$  (Sect. 579 3.3). However, isotopic characterization experiments are typically conducted 580 at much different temperature, pressure, and  $\delta D(H_2O)$  conditions than would 581 occur in an ice sheet. It is also possible that  $CH_4$  is produced in situ by some 582 abiotic process, however these mechanisms appear to require a high concen-583 tration of organic precursor (Jugold et al., 2012; Wang et al., 2017). 584

# 585 4.6. A deposition source of excess CH<sub>4</sub>

Instead of being produced in the ice sheet, excess  $CH_4$  may instead be carried from a  $CH_4$  source to the ice sheet by some agent capable of absorbing hydrocarbons like clay minerals in dust, black carbon (BC), or organic carbon all of which are known to be abundant in the Greenlandic ice cores (Biscaye et al., 1997; Svensson et al., 2000).

<sup>591</sup> Dust and clay minerals in the GISP2 and GRIP ice cores are well doc-<sup>592</sup> umented (Mayewski et al., 1997; Rasmussen et al., 2014; Schüpbach et al., <sup>593</sup> 2018). Provenance of the dust is primarily from the Takla Makan desert in <sup>594</sup> West China (Biscaye et al., 1997; Svensson et al., 2000; Bory et al., 2003).

In parts of this region,  $CH_4$  diffuses through the soil from underlying fossil 595 fuel reservoirs (Etiope and Klusman, 2002; Etiope et al., 2008) providing a 596 viable source for  $CH_4$  adsorption. While estimates of the adsorptive capacity 597 of clay for abundances found in the GISP2 ice samples (calculated following 598 Ji et al. 2012) show that this is a feasible mechanism, it is only feasible under 599 ideal conditions for adsorption, retention of  $CH_4$  during transport, and with 600 efficient desorption during sample extraction (Appendix D, S. Table D.1). 601 Many factors could limit the adsorptive capacity of clays such as the partial 602 pressure of  $CH_4$ , the temperature of the clays, and the presence of water or 603 other species during adsorption. Once in the atmosphere (transport time of 604 days) and while still in contact with the atmosphere in the firm (centuries) the 605 dust is in a much lower  $CH_4$  environment and  $CH_4$  would likely be released 606 from the dust. Further, our estimates of the isotopic signature of excess CH<sub>4</sub> 607  $(\delta D(CH_4)_{xs} = -293\%)$  (Sect. 3.3) do not support this mechanism because 608 our estimate is significantly more negative than typical emissions from seeps 609  $(\delta D(CH_4))$  values of ~-185 to -200‰, Quay et al. 1999; Etiope et al. 2007; 610 Fischer et al. 2008). 611

A pyrogenic source, such as wildfires (-195 to -255<sup>\overline</sup>, Quay et al. 1999; 612 Snover et al. 2000), can not be definitively excluded by our estimates of 613  $\delta D(CH_4)_{xs}$ . In this case,  $CH_4$  is more likely to be adsorbed and transported 614 to the ice sheet by BC or organic matter. However, measurements of BC and 615 organic matter are currently not available from a Greenlandic ice core. Iden-616 tifying a source for excess  $CH_4$  would benefit from estimate of  $\delta^{13}C(CH_4)_{xs}$ , 617 but no record currently exists of  $\delta^{13}C(CH_4)$  during DO-events from a Green-618 landic ice core. 619

#### 5. Considerations for atmospheric reconstructions

Rapid changes of  $[CH_4]$  during the last glacial period, specifically those 621 corresponding with D-O events, have been used extensively in the develop-622 ment of age scales for ice cores (Blunier et al., 1998; Brook et al., 2000; 623 Kindler et al., 2014; Buizert et al., 2015). At the onset of D-O events,  $[CH_4]$ 624 increased by 60-220 ppb (Baumgartner et al., 2014), a large value in com-625 parison to the impact of excess  $CH_4$  on the ice core record (less than 40 626 ppb) implying that excess  $CH_4$  probably has not affected  $[CH_4]$ -based age 627 scales. One possible exception is DO-2, for which  $[CH_4]$  only changed by 628 20-35 ppb (Baumgartner et al., 2012, 2014; Schilt et al., 2010). This event is 629 important for gas-based chronologies because of the lack of other significant 630

variations around this time period. Ice core records of  $[CH_4]$  have also been used to reconstruct past radiative forcing with regards to the inferred climate changes of D-O cycles (Petit et al., 1999). The relatively small impact of excess  $CH_4$  on the ice core  $[CH_4]$  record would not significantly alter these interpretations.

The geographic distribution of  $CH_4$  sources in the past has been recon-636 structed from the difference in concentration between records of  $[CH_4]$  from 637 Greenlandic and Antarctic ice cores (referred to as the "Inter-Polar Differ-638 ence", or IPD, Chappellaz et al., 1997; Dällenbach et al., 2000; Brook et al., 639 2000; Mitchell et al., 2013; Baumgartner et al., 2012; Beck et al., 2018). Dur-640 ing the last glacial cycle, the IPD ranged from  $\sim 10-50$  ppb with the Northern 641 Hemisphere always having greater  $[CH_4]$  (Baumgartner et al., 2014). Excess 642 CH<sub>4</sub>, which is only observed in Greenlandic ice core samples, has likely caused 643 the IPD to be overestimated during dusty time periods in Greenland. Since 644 the impact of excess  $CH_4$  on the Greenlandic records is of the same magnitude 645 as the IPD, it will be critical to account for this effect. 646

Excess  $CH_4$  also appears to have a large influence on the measured iso-647 topic composition of  $CH_4$  (Sect. 2.3). As discussed in Sect 3.3, assuming 648 an isotopic signature ( $\delta D(CH_4)_{xs}$ =-293‰) similar to natural sources, the 649 excess  $CH_4$  contribution can account for much of the observed variability 650 in the NGRIP  $\delta D(CH_4)$  record (Bock et al., 2010b). Accordingly, some of 651 the  $\delta D(CH_4)$  variability in Bock et al. (2010b) is likely due to excess  $CH_4$ 652 and the conclusions of Bock et al. (2010b) should be confirmed using an 653 Antarctic ice core. Although, a record of  $\delta^{13}C(CH_4)$  has yet to be measured 654 from a Greenlandic ice core during a period with dusty ice,  $\delta^{13}C(CH_4)$  will 655 likely also be affected by excess  $CH_4$ . Assuming an isotopic signature for 656 excess CH<sub>4</sub> of  $\delta^{13}C(CH_4)_{xs}$  equal to microbially produced CH<sub>4</sub> (~-60 ‰, 657 Quay et al. 1999; Bock et al. 2017), the impact of excess  $CH_4$  may be up to 658  $\sim 1.5\%$ . This magnitude of impact is significant when compared to centen-659 nial to millennial-scale variations as recorded in the Antarctic Vostok and 660 EDML ice cores (Möller et al., 2013). 661

Recently, centennial-scale variability in  $[CH_4]$  during the last glacial period was identified in the WAIS Divide and Fletcher Promontory ice cores from Antarctica (Rhodes et al., 2017). These records confirmed the variability previously measured in the NEEM ice core (Chappellaz et al., 2013). The peak-to-peak magnitude of this variation was cited to be 8-12 ppb in the ice core record which was estimated to represent 8-24 ppb variations in the atmosphere (Rhodes et al., 2017). This is smaller than the impact of

excess  $CH_4$  observed in Greenlandic ice cores meaning that centennial-scale 669 variations could be confused for or masked by excess CH<sub>4</sub>. We stress that we 670 do not question the existence of the centennial-scale atmospheric variations 671 for two reasons. First, excess  $CH_4$  was absent in the discrete WAIS Divide 672 samples (equivalent to contamination of  $-2 \text{ ppb } \pm 2 \text{ ppb}$ , n=82), which closely 673 replicated all modes of variability in the continuous  $[CH_4]$  measurements dis-674 cussed in Rhodes et al. (2017). Second, the corrected GISP2 and NEEM 675 discrete records also reproduce the centennial-scale variability in  $[CH_4]$  ob-676 served in the WAIS Divide record during DO-12 (Fig. 6, Sect. 3.2). The 677 robust centennial-scale variations in both Greenlandic and Antarctic ice cores 678 are important for the future development of high-precision gas age chronolo-679 gies (Mitchell et al., 2013; Lee et al., 2018) and for understanding the climatic 680 links to these variations of the  $CH_4$  cycle in the past. 681

#### 682 6. Implications for extremophiles

While no direct evidence of active microbes capable of producing green-683 house gases in "normal" ice has been reported, elevated concentrations have 684 been observed for some biogenically produced gases such as  $CO_2$ ,  $N_2O_2$ , and 685  $CH_4$  (Sowers, 2001; Flückiger et al., 2004; Campen et al., 2003; Rhodes et al., 686 2013). Furthermore, several lines of circumstantial evidence support in situ 687  $CH_4$  production, including the general association of high cell counts with 688 high concentrations of dust (Abyzov et al., 1998; Tung et al., 2005; Rohde 689 et al., 2008; Miteva et al., 2009, 2016). Viable cells in the GISP2 ice core 690 have been estimated to account for 2.5-15% of the total cells present (Miteva 691 et al., 2009, 2015), although methanogens have not been identified in normal 692 ice samples (Tung et al., 2005; Rohde et al., 2008). One sample with an 693 extremely high concentration of cells, 2238 m depth in the GISP2 ice core 694 (Tung et al., 2005), was coincidentally among discrete  $[CH_4]$  samples inferred 695 to be affected by excess  $CH_4$  (Sect. 2.1). 696

The possibility of in situ CH<sub>4</sub> production could be tested with dust rich samples of younger ages (shallower depths), because the quantity of excess CH<sub>4</sub> should increase with age (Sect. 4.5). However, in GISP2 samples ranging from 42-75 ka we observed a consistent relationship between excess CH<sub>4</sub> and Ca<sup>2+</sup> implying that CH<sub>4</sub> is not produced in situ at these depths (Sect. 3.4 and 4.5). If we assume no in situ production is observed because of nutrient limitation and that 95-99% of the limiting precursor for methanogenesis was consumed by the age of our youngest sample, the representative e-folding
time for the reaction is at most 9,000-14,000 years.

Production of biogenic gases in ice cores has been previously estimated 706 by Price and Sowers (2004), Tung et al. (2005), and Rohde et al. (2008). 707 Their estimates were based upon the idea that microbes in the ice sheet are 708 only active enough to sustain themselves but not to reproduce. This implies 709 that  $CH_4$  is produced continuously in the ice core at constant rate. Following 710 their calculation and using their empirically derived production rates for ice 711 at  $-28^{\circ}$  C ( $\sim 5 \times 10^{-8}$  (g C-CH<sub>4</sub>/g C-biomass)·yr<sup>-1</sup>), the estimated carbon 712 mass of methanogens (19 femtograms C/cell, Price and Sowers 2004; Tung 713 et al. 2005), the estimated percent of cells which are methanogens in normal 714 ice (1/300), Price and Sowers 2004; Tung et al. 2005), the cell count at 2238 715 m depth ( $\sim 10^5$  cells/mL, Tung et al. 2005), and the estimated percent of 716 cells which are healthy (Miteva et al., 2009) yields an expected production 717 of  $\sim 0.00005$  picomoles CH<sub>4</sub>/g ice since 35,000 years. This estimate is much 718 smaller than the estimates of  $n_{xs}^*$  of up to ~0.01 picomoles CH<sub>4</sub>/g ice in Sect. 719 3.2. Additionally, their assumption of continuous production is inconsistent 720 with the observed constant ratio of  $n_{xs}^*$  and  $Ca^{2+}$  in the GISP2 ice core (Sect. 721 3.2). If the excess CH<sub>4</sub> we observe is due to metabolism within the ice sheet, 722 then microbial metabolism in normal ice is more vigorous than required for 723 simply sustaining life. 724

## 725 7. Conclusions

We discuss a new process able to distort the atmospheric record preserved 726 in ice cores by elevating the measured concentration of  $CH_4$ . This process 727 is related to a commonly used measurement technique, where the sample 728 is melted for prolonged periods (15-30 minutes) to liberate air from within 729 the sample. The elevated values were observed for "normal" ice core samples 730 (ice core samples which are not affected by melt layers or entrained sediment) 731 and differs from other non-atmospheric processes such as the very brief spikes 732 resulting from in situ processes observed by (Rhodes et al., 2013) and from 733 annual-layer trapping signals (Rhodes et al., 2013, 2016), which are localized 734 reversals of the depth-age relationship. This additional  $CH_4$ , referred to 735 as "excess  $CH_4$ ", was only observed in samples with high concentrations 736 of dust and impurities and not observed in Antarctic ice core samples and 737 Greenlandic ice core samples with low dust concentrations. Several potential 738 sources of CH<sub>4</sub> are proposed, although none perfectly match our observations. 739

The possible mechanisms which we consider the most likely explanations for 740 the excess  $CH_4$  include the transport of  $CH_4$  adsorbed onto dust or BC 741 particles from remote regions and in situ production of  $CH_4$  on or in dust 742 particles. However, our observations cannot exclude the mechanism of abiotic 743 in vitro production (i.e.  $CH_4$  produced during the melt-extraction step of 744 sample analysis). Both of our preferred pathways focus on the adsorption 745 of  $CH_4$  onto the particle and subsequent desorption of  $CH_4$  during the melt-746 extraction step of sample analysis when liquid water is present. Since in 747 situ methanogenesis would gradually increase the abundance of  $CH_4$  in the 748 ice sheet, measurement of younger ice could provide valuable information to 749 distinguish between the two proposed mechanisms. 750

As future ice core records of  $CH_4$  gain precision and resolution, a more 751 direct approach to measuring or negating the effects of excess CH<sub>4</sub> will need 752 to be developed. One possible way forward could be to measure a suite of 753 samples with a "dry" extraction technique where air is extracted by mechan-754 ically crushing the ice or through sublimation (Etheridge et al., 1996, 1998; 755 Sapart et al., 2011; Schmitt et al., 2011), which may not be affected by excess 756  $CH_4$  in the same way because the sample is not melted. Comparing to  $[CH_4]$ 757 records measured with a melt-extraction technique ("wet" extraction) could 758 both test our proposed ideas about the desorption of  $CH_4$  in the presence of 759 liquid water and provide a reference for Northern Hemisphere CH<sub>4</sub> concen-760 trations during dusty intervals. No evidence of excess  $CH_4$  was observed in 761 records measured with continuous flow analysis, potentially due to the short 762 time period before the gas is separated from the liquid stream. Therefore, an 763 independently calibrated continuous  $[CH_4]$  record from a Greenlandic ice core 764 may also provide a reference, although currently no such record is available. 765 While it is clear that excess  $CH_4$  will need to be accounted for when 766 interpreting records of  $[CH_4]$  and the stable isotopes of  $CH_4$ , the presence 767

<sup>768</sup> of excess  $CH_4$  may be evidence of microbial activity occurring within the <sup>769</sup> Greenland ice sheet. The abundance of cells has been observed to vary in <sup>770</sup> ice cores with the concentration of dust (Abyzov et al., 1998; Tung et al., <sup>771</sup> 2005; Miteva et al., 2016), implying that an empirical relationship also with <sup>772</sup> excess  $CH_4$ . Methanogenesis in such a harsh environment tests the limits of <sup>773</sup> life, possibly providing an analogue for early life on Earth or possible life on <sup>774</sup> other planets.

# 775 Acknowledgements

This work was funded by grants from the US National Science Founda-776 tion PIRE award 0968391. Research performed at the University of Bern has 777 received funding from the European Research Council (ERC) under the Eu-778 ropean Union s Seventh Framework Programme FP7/2007-2013 ERC grant 779 226172 (ERC Advanced Grant Modern Approaches to Temperature Recon-780 structions in Polar Ice Cores (MATRICs)) and the Swiss National Science 781 Foundation. We thank Jonas Beck and Barbara Seth for discussion and their 782 expertise in the measurement of the stable isotope composition of  $CH_4$ . 783

# 784 Data Availability

Datasets related to this article can be found at: https://www.ncdc. noaa.gov/paleo/study/27610.



Figure 1: Comparison of  $[CH_4]$  histories from Greenlandic ice cores: (a) NGRIP (Baumgartner et al., 2014), (b) GISP2 (Brook et al. 1996, 2000 and previously unpublished measurements will be made available at NOAA National Centers for Environmental Information (Link), (c) NEEM continuous (Chappellaz et al., 2013), and (d) GRIP (Blunier and Brook, 2001; Flückiger et al., 2004; Landais et al., 2004) to the WAIS continuous record (Rhodes et al., 2015), and to (e)  $Ca^{2+}$  concentrations (Rasmussen et al., 2014; Schüpbach et al., 2018). All [CH<sub>4</sub>] records have been translated onto the NGRIP ice age scale. DO-events as expressed by [CH<sub>4</sub>] are labeled in blue with parentheses, and as expressed in  $Ca^{2+}$  are labeled in black. Gray bars highlight periods of high  $Ca^{2+}$  concentrations. Hatched boxes indicate intervals where discrete records diverge from the WAIS Divide and NEEM continuous records.



Figure 2: Records of (a) NGRIP [CH<sub>4</sub>] (Baumgartner et al., 2014), (b)  $\delta D(CH_4)$  from NGRIP (Bock et al., 2010b) plotted on the NGRIP GICC05 ice age scale, and (c) NGRIP Ca<sup>2+</sup> (Rasmussen et al., 2014; Schüpbach et al., 2018). [CH<sub>4</sub>] records from the NEEM (Chappellaz et al., 2013) and NGRIP ice cores show inconsistencies between records. Excursions observed in the stable isotope record of CH<sub>4</sub> from the NGRIP ice core occur at similar depths as the discrepancies in [CH<sub>4</sub>] and in ice with high concentrations of Ca<sup>2+</sup>. DO-events as expressed by [CH<sub>4</sub>] are labeled in blue, and as expressed by Ca<sup>2+</sup> are labeled in black.



Figure 3: (a)  $[CH_4]$  (b)  $\Delta CH_4$  and (c) excess CH<sub>4</sub> from the GISP2 ice core are plotted against depth. (a) includes the first set of GC measurements from each sample ( $[CH_4]$ , gray circles), the second set ( $[CH_4]^*$ , open gray circles), and a "corrected" value (green diamonds). (d) Calcium concentrations from the GISP2 are plotted for comparison (Mayewski et al., 1997).



Figure 4:  $CH_4$  results from the NEEM ice core are plotted against depth, same as Fig. 3. The NEEM  $Ca^{2+}$  record is sub-sampled from an ultra-high resolution CFA dataset (Schüpbach et al., 2018).



Figure 5: Regression of  $n_{xs}^*$  against the quantity of calcium in GISP2 and NEEM samples (Mayewski et al., 1997; Schüpbach et al., 2018) following methods of York et al. (2004). For GISP2 samples with an age between 42 and 50 ka (gray dots), the skill of the regression is  $R^2=0.78$  with  $5.2 \pm 0.5 \mu$ moles (95% CI) of excess CH<sub>4</sub> per mole of calcium, and  $R^2=0.64$  with  $7.5 \pm 2.0 \mu$ moles of excess CH<sub>4</sub> per mole of calcium for NEEM samples. Older GISP2 samples, dating between 72-75 ka, are plotted as red dots.



Figure 6: Measured  $[CH_4]$  and concentrations after an ad hoc correction for excess  $CH_4$  from the GISP2 (orange) and NEEM (Green) ice cores. Discrete measurements are compared to the WAIS Divide and NEEM continuous records (black and gray, respectively). Both the GISP2 and NEEM data were synchronized to the WD2014 age scale (Buizert et al., 2015).



Figure 7: A modeled ice core history of  $\delta D(CH_4)$  with a two-component mixing model with end-members of atmospheric air and excess CH<sub>4</sub>. Black lines and circles are measurements of (a) [CH<sub>4</sub>] (Baumgartner et al., 2014), (b)  $\delta D(CH_4)$  (Bock et al., 2010b), and (c) [Ca<sup>2+</sup>] (Rasmussen et al., 2014) from the NGRIP ice core. Red line in panel (a) is the atmospheric component in the model. Panel (b) also shows model results for  $\delta D(CH_4)_{atm}$  (dashed) and  $\delta D(CH_4)_{model}$  (solid) based on an empirical relationship between enrichments of [CH<sub>4</sub>] and concentrations of Ca<sup>2+</sup>.



Figure 8: Inhibition experiments. Five GISP2 sample depths were measured in replicate; two dust-rich sample depths and three low-dust samples. One replicate of each sample depth was poisoned with HgCl<sub>2</sub> (orange) while the other was used as a control (blue). (a) Filled squares are measurements after the first extraction ([CH<sub>4</sub>]), open squares are measurements after the second extraction ([CH<sub>4</sub>]\*). [CH<sub>4</sub>] values match previous measurements of [CH<sub>4</sub>] from Grachev et al. (2009) (gray squares). (b) The difference between the first and second set of measurements ( $\Delta$ CH<sub>4</sub>) (circles) show a good correspondence with the dust concentration at those sample depths (open diamonds).

: Coefficient of determination ( $\mathbb{R}^2$ ) of release/production or $n_{xs}^*$ in dust-rich GISP2 and NEEM samples compared is of chemical species in the ice sample (Mavewski et al., 1997; Schüpbach et al., 2018). Interpolated GISP2 ion	rations are a weighted mean of the 20 cm binned average values. NEEM ion concentrations and dust counts are	pled for the depth range of our NEEM samples (Schüpbach et al., 2018). Statistical p-values for correlation are all		$ $ $n   N_0 + NH^+   V^+   M_0^2 +   C_0^2 +   C_1 -   NO^-   CO^2 -   D_{116} + \mu^-$
Table 1: Coeffici to moles of chem	concentrations ar	sub-sampled for 1	< 0.0001.	

	u	$Na^+$	$\mathrm{NH}_4^+$	$\mathrm{K}^+$	$\mathrm{Mg}^{2+}$	$Ca^{2+}$	$Cl^{-}$	$\rm NO_3^-$	$\mathrm{SO}_4^{2-}$	Dust #
$T_{melt}=2$	6° C									
GISP2	42	0.67	0.20	0.66	0.75	0.78	0.58	0.33	0.67	
NEEM	27					0.64				0.59
$T_{melt}=0$	C °									
GISP2	42	0.25	0.06	0.28	0.34	0.37	0.16	0.12	0.25	
NEEM	27					0.54				0.49

 $_{787}$  Appendix A.  $\rm CH_4$  records on gas-age scales

#### <sup>788</sup> Appendix B. Calculation of CH<sub>4</sub> partitioning constant

During our gas extraction process some air is dissolved into the melt water 789 and is not expelled during the refreeze step, unlike in systems which flush the 790 melt water with a carrier gas or slowly refreeze the melt water. Since  $CH_4$  is 791 more soluble than nitrogen or oxygen, the major species in air, the measured 792  $CH_4$  concentration ([CH<sub>4</sub>]) is lower than when the air was trapped in the ice 793 core. Dissolution of gases into the melt water is a kinetic process and due 794 to the short melt-refreeze cycle (approximately 30 minutes) the uptake of 795 gases into the melt water is likely halted before thermodynamic equilibrium 796 is reached. This means the dissolved  $CH_4$  is likely lower than the capacity 797 of the melt water (undersaturated) and an empirical correction is needed 798 to accurately estimate the quantity of  $CH_4$  trapped in the refrozen sample. 799 Previous studies estimated that dissolved  $CH_4$  accounts for  $\sim 1.7\%$  of the 800 total  $CH_4$  from an ice core sample for the OSU system (Grachev et al., 2009; 801 Mitchell et al., 2013). Although this estimate was calculated in a different 802 way, it agrees well with estimates made here. 803

The effects of differential solubility will cause  $[CH_4]$  in the headspace to increase after the second melt-refreeze. The mean  $[CH_4]$  value of the second measurement set  $([CH_4]_{gas}^*)$  minus the mean value of the first measurement set  $([CH_4]_{gas})$  is referred to as  $\Delta CH_4$ .

$$\Delta CH_4 = [CH_4]^*_{gas} - [CH_4]_{gas} \tag{B.1}$$

Positive  $\Delta CH_4$  values are observed in the vast majority of our samples 808 (Fig. 3 and 4) including BFI samples and samples assumed to be unaffected 809 by excess CH<sub>4</sub>. An increase in concentration is caused by the decrease in sam-810 ple pressure in the flask as sample air is consumed during the first sequence 811 of GC measurements (consuming  $\sim 60\%$  of the sample air). The reduction in 812 pressure causes  $CH_4$  to degas during the second melt-refreeze cycle resulting 813 in higher  $[CH_4]$  values for the second set of measurements compared to the 814 first set of measurements. In these samples,  $\Delta CH_4$  is related to the total 815 air content (TAC),  $[CH_4]$ , the size of the sample, the relative solubility of 816 CH<sub>4</sub> compared to major air components, and the relative diffusion rates and 817 extent of progress toward solubility equilibrium of  $CH_4$  in comparison to  $N_2$ 818 and  $O_2$  during the first melt-extraction and expulsion of gases during the 819 subsequent refreeze. 820

To estimate the amount of  $CH_4$  left in the solution/ice after the first 821 refreeze, we define and empirically estimate the "partitioning constant", 822  $K_{partition}$ .  $K_{partition}$  is the partial pressure of  $CH_4$  in the headspace divided by 823 the concentration of the  $CH_4$  trapped in the ice following the first extraction 824 (units of MPa $\cdot$ (mol/kg)<sup>-1</sup> and is calculated for each sample. This parameter 825 is similar to Henry's constant, which describes the partial pressure of gas 826 over the dissolved species in water under the conditions of thermodynamic 827 equilibrium. In this definition, and in the absence of release/production of 828  $CH_4$  during analysis, Henry's constant places a lower limit on the value of 829  $K_{partition}$  because in the first extraction  $CH_4$  is being absorbed into melt 830 water. 831

The second melt-refreeze cycle begins closer to equilibrium and we assume that the flux of  $CH_4$  out of solution during this step brings  $[CH_4]$  near equilibrium. If equilibrium is not reached during the second melt-refreeze, then our calculation will underestimate  $n_{xs}^*$  (Appendix C). Given this assumption, the total number of moles of  $CH_4$  in the flask, both the dissolved and gas phase, can be estimated and  $K_{partition}$  can be calculated by the following system of equations:

$$n_{total} = n_{ice\,core} = n_{gas} + n_{aq} \tag{B.2}$$

$$n_{total}^{*} = n_{gas}^{*} + n_{aq}^{*} = f \cdot n_{gas} + n_{aq}$$
(B.3)

$$n_{gas} = [CH_4]_{gas} \cdot \frac{m \cdot TAC \cdot P_{STP}}{R \cdot T_{STP}}$$
(B.4)

$$n_{gas}^* = [CH_4]_{gas} \cdot \frac{m \cdot TAC^* \cdot P_{STP}}{R \cdot T_{STP}} \tag{B.5}$$

$$[CH_4]_{aq} = \frac{n_{aq}}{m} \tag{B.6}$$

$$K_{partition} = \frac{p}{[CH_4]_{aq}} \tag{B.7}$$

$$H = \frac{p^*}{[CH_4]_{aq}^*}$$
(B.8)

$$n_{aq}^{*} = [CH_{4}]_{aq}^{*} \cdot m = m \cdot \frac{p_{CH4}^{*}}{H}$$
(B.9)

Variables demarcated with "\*" indicate they are associated with the second melt-refreeze cycle and second set of measurements. The sample mass is given as "m" in units of grams. "R" is the ideal gas constant (8.314

 $J \cdot mol^{-1} \cdot K^{-1}$ ). TAC is in units of cc air (STP)/gram ice and is a byproduct 842 of  $[CH_4]$  measurements. "n" is the number of moles of  $CH_4$  with the phase 843 or origin identified by the subscript. "p" is the partial pressure of  $CH_4$  in 844 the headspace while the sample is melted (Pa). In eqn. B.4 and B.5, "n<sub>aas</sub>" 845 and " $n_{aas}^*$ " are the number of moles of  $CH_4$  in the gas phase after the first 846 and second melt-refreeze extraction and are calculated from the TAC and 847 the measured  $[CH_4]$  of the sample. In eqn. B.8 and B.9, "H" is the Henry's 848 Law solubility constant of CH<sub>4</sub> (for water at  $0^{\circ}$  C, H=43.3 MPa·(mol/kg)<sup>-1</sup>; 849 at 26° C, H=73.3 MPa·(mol/kg)<sup>-1</sup>) (Lide, 2004). The variable f is the frac-850 tion of air remaining in the headspace after the first set of measurements is 851 complete and is calculated from the pressure of the last measurement of the 852 set and an estimate of volume of the flask. 853

p can not be directly measured but can be estimated by the ideal gas law 854 which is dependent on the temperature of air within the flask as the sample 855 is melted. This temperature is not well known and changes throughout the 856 melt-refreeze process. We tested a range of temperatures from a lower limit 857 of  $0^{\circ}$  C to an upper limit of  $26^{\circ}$  C, the measured temperature of a sample 858 immediately after the 30 minute melt cycle. In the OSU system, under 859 this temperature and pressure range  $CH_4$  overwhelmingly exists as in the gas 860 phase, rather than in the dissolved state, and assumptions about temperature 861 have limited impact on our results. 862

Equations B.2-B.9 simplify to solve for  $K_{partition}$ :

$$K_{partition} = \frac{n_{gas}}{n_{gas}^* \cdot (1 + m \cdot R \cdot T_{melt} \cdot V_{headspace}^{-1} \cdot H^{-1}) - f \cdot n_{gas}} \cdot \frac{m \cdot R \cdot T_{melt}}{V_{headspace}}$$
(B.10)

Where  $T_{melt}$  is the temperature of gas during the melt-refreeze cycle (either 0° C or 26° C), and  $V_{headspace}$  is the volume of the headspace in the flask.  $T_{melt}=26^{\circ}$  C, is based on measurements of the temperature of melt water following a third melt-extraction and is considered the maximum temperature a sample reaches before re-immersion into the cold-bath for refreezing.

 $K_{partition}$  was calculated for each sample individually (S. Fig B.2). Since this is an empirical quantification, any process which could affect the aqueousgas exchange of CH<sub>4</sub> during the extraction process (such as the ion activity, sample water temperature, or the expulsion of dissolved gases during freezing) is incorporated in this term.

In general, our determinations of  $\mathbf{K}_{partition}$  are higher than equilibrium 874  $(T=)^{\circ}$  C) (Lide, 2004) indicating that dissolution of CH<sub>4</sub> into the water was 875 incomplete during the first extraction. However, enough  $CH_4$  is dissolved that 876 under the reduced pressure during the second gas extraction out-gassing of 877 CH<sub>4</sub> occurs. The exceptions are GISP2 and NEEM samples with high con-878 centrations of  $Ca^{2+}$ . In both of these cases,  $\Delta CH_4$  indicates that more  $CH_4$ 879 out-gassed from the melt water during the second melt-refreeze cycle than 880 would be possible even if  $CH_4$  dissolution had reached equilibrium during the 881 first melt-extraction. 882

We categorize samples into groups based on their drill site as well as if  $K_{partition}$  is less than equilibrium (H). A baseline  $K_{partition}$  for each group  $(\overline{K}_{partition}, \text{Table B.1})$ , calculated as the mean of each grouping, describes the typical partitioning of CH<sub>4</sub> between dissolved and gas phases after the first extraction.  $\overline{K}_{partition}$  can be used to estimate an expected  $\Delta \text{CH}_4$ . The difference between the expected  $\Delta \text{CH}_4$  and the measured  $\Delta \text{CH}_4$  is an estimate of  $n_{xs}^*$  (Appendix C).

For low-dust GISP2 ice samples, those in which  $K_{partition}$  is greater than 890 H, the mean difference between measured  $\Delta CH_4$  and the expected value cal-891 culated from  $\overline{K}_{partition}(T_{melt} = 0^{\circ} C)$  is 1.2 ppb  $\pm$  2.4 ppb, n=46 (Fig. B.3). 892 The non-zero difference is because of the non-linear relationship between 893  $K_{partition}$  and  $\Delta CH_4$ . For WAIS Divide and bubble free ice samples, which 894 895 we believe are unaffected by excess  $CH_4$ , difference between the measured and expected  $\Delta CH_4$  is 3.5 ppb  $\pm$  4.9 ppb (n=82) and -0.1 ppb  $\pm$  5.0 ppb 896 (n=69), respectively. The uncertainty is similar to the combined uncertainty 897 of the first and second set of measurements. 898

Temp.	NIST	WAIS	SPICE	GISP2	GISP2	NEEM	NEEM	BFI
				low-	high-	low-	high-	
				dust	dust	dust	dust	
0° C	39.6	43.9	42.9	49.3	30.2	45.8	25.7	72.4
$26^{\circ} \mathrm{C}$	73.3	61.6	57.8	79.8	49.1	89.9	38.6	114.1

Table B.1: Calculated  $\overline{K}_{partition}$  for different ice cores (MPa·(mol/kg)<sup>-1</sup>). NIST value is the Henry's Constant for CH<sub>4</sub> (Lide, 2004).

### <sup>899</sup> Appendix C. Calculation of excess $CH_4$

The mass balance equation describing the second melt-refreeze cycle (Eqn. B.3) can be rewritten to include the potential release/production of CH<sub>4</sub>  $n_{xs}^*$ ).

$$(f \cdot n_{gas} + n_{aq}) + n_{xs}^* = n_{gas}^* + n_{aq}^*$$
(C.1)

The first two terms on the left side of this equation describe the quantity of CH<sub>4</sub> remaining in the flask after the first set of measurements and before the second melt-refreeze step. The right side of the equation describes the quantity of CH<sub>4</sub> after the second melt-refreeze. The difference between the two sets of terms gives us the quantity of CH<sub>4</sub> released or produced during the second melt-refreeze step  $(n_{xs}^*)$ .

The fraction of CH<sub>4</sub> trapped in the refrozen melt-water following the two melt-refreeze steps ( $n_{aq}$  and  $n_{aq}^*$ ) is determined from the empirically derived  $\overline{K}_{partition}$  and H, respectively.

$$n_{aq} = m \cdot \frac{p}{\overline{K}_{partition}} \tag{C.2}$$

$$n_{aq}^* = m \cdot \frac{p^*}{H} \tag{C.3}$$

As in Sect. Appendix B, 'm' represents the mass of the sample, 'p' is the partial pressure of CH<sub>4</sub> in the headspace during the melt-extraction, and H is the equilibrium solubility constant.

From this set of equations,  $n_{xs}^*$  can be solved following:

$$n_{xs}^* = n_{gas}^* \cdot \left(1 + \frac{m \cdot A}{H}\right) - n_{gas} \cdot \left(f + \frac{m \cdot A}{\overline{K}_{partition}}\right) \tag{C.4}$$

<sup>916</sup> Where A is the conversion factor between p and  $n_{gas}$  (A=  $R \cdot T_{melt} \cdot V_{headspace}^{-1}$ ). <sup>917</sup> Two main assumptions have been made in order to calculate  $n_{xs}^*$ . First, <sup>918</sup> the distribution between gas and dissolved phases of CH<sub>4</sub> reaches equilibrium <sup>919</sup> during the second melt-refreeze. If CH<sub>4</sub> is not able to completely degas from <sup>920</sup> solution and reach equilibrium during this step, than some aqueous CH<sub>4</sub> is

unaccounted for and our estimates of  $n_{xs}^*$  are too low. The second assumption 921 is the temperature of the water during the melt-refreeze step which deter-922 mines equilibrium solubility (H). As in the case of  $\overline{K}_{partition}$ , the calculation 923 of  $n_{aq}^*$  was repeated assuming  $T_{melt}=0^\circ$  C and 26° C. We also repeat the cal-924 culation of  $n_{xs}^*$  assuming no dissolution of  $CH_4$  (H=0, a maximum estimate 925 for  $n_{xs}^*$ ) and repeat the calculation assuming that gases reach thermodynamic 926 equilibrium during the first melt-refreeze ( $K_{partition} = H$ , a minimum estimate 927 of  $n_{rs}^{*}$ ). Typically, the difference between the maximum scenario and our 928 estimate was small (0.33 picomoles given  $T_{melt}=26^{\circ}$  C, and 0.83 picomoles 929 given  $T_{melt}=0^{\circ}$  C) and is larger at low quantities of  $n_{xs}^{*}$ . At low values of  $n_{xs}^{*}$ 930 some of  $\Delta CH_4$  is attributed to out-gassing of  $CH_4$ , however in the maximum 931 scenario  $\Delta CH_4$  is solely attributed to excess  $CH_4$ . 932

#### <sup>933</sup> Appendix D. Calculation of adsorptive capacity

An estimate of the concentration of dust in the GISP2 ice core was given 934 in Ram and Koenig (1997) and Ram et al. (2000). We use these data as 935 a maximum estimate for the abundance of clay minerals in the GISP2 ice 936 samples. Adsorption of  $CH_4$  by clays depends on the mineralogy. Clay in the 937 GISP2 and GRIP ice cores was characterized for several periods during the 938 last glacial period and found to be dominated by illite (Biscaye et al., 1997; 939 Svensson et al., 2000; Ujvári et al., 2015). The abundance of illite relative 940 to other clay minerals was relatively constant throughout the time period 941 studied. Estimation of the adsorption capacity follow Ji et al. (2012), and 942 use the amount of dust in the sample, the clay composition of the dust, and 943 by assuming a partial pressure and temperature during adsorption (Table 944 D.1). 945

<sup>946</sup> Under ideal conditions, with high partial pressures of  $CH_4$  during adsorp-<sup>947</sup>tion, the resulting adsorptive capacity of clays in the GISP2 ice core would <sup>948</sup>be greater than the calculated  $n_{xs}^*$ . Such conditions may exist in soils with <sup>949</sup>seepage of geologic  $CH_4$ . However, our calculated value of  $n_{xs}^*$  only accounts <sup>950</sup>for excess  $CH_4$  released/produced during the second melt extraction and not <sup>951</sup>the total excess  $CH_4$  that could be released/produced given additional time. <sup>952</sup>Values given in Table D.1 are therefore a maximum value.



Figure A.1: Comparison of  $[CH_4]$  histories from Greenlandic ice cores: (a) NGRIP (Baumgartner et al., 2014), (b) GISP2 (Brook et al. 1996, 2000 and previously unpublished measurements available at https://www.ncdc.noaa.gov/paleo/study/27610, (c) NEEM (Chappellaz et al., 2013), and (d) GRIP (Blunier and Brook, 2001; Flückiger et al., 2004; Landais et al., 2004) to the WAIS Divide continuous  $[CH_4]$  record Rhodes et al. (2015). The WAIS Divide  $[CH_4]$  values have been shifted to account for the interpolar concentration difference of  $[CH_4]$ . Greenland records are plotted on their respective GICC05 gas age scales (Rasmussen et al., 2013; Kindler et al., 2014; NEEM Community Members, 2013). The WD2014 gas age scale has been reduced by a constant 0.64% following (Buizert et al., 2015) to translate the WAIS Divide  $[CH_4]$  record to the GICC05 age scale. Hatched boxes indicate intervals where discrete records diverge from continuous records.



Figure B.2: Measured partitioning constant ( $K_{partition}$ ) of different ice cores. For the GISP2 and NEEM ice cores, orange bars represent dust-rich ice samples where excess CH<sub>4</sub> was observed and blue bars represent low-dust samples where excess CH<sub>4</sub> was absent. Henry's constant for CH<sub>4</sub>, (vertical dashed lines) was calculated assuming T=26° C (Lide, 2004). Values smaller than Henry's constant imply release or production of CH<sub>4</sub> during the extraction process.



Figure B.3: Measured minus expected  $\Delta CH_4$  for different low-dust ice samples used as a baseline for  $\overline{K}_{partition}$ . These samples were assumed to have no excess  $CH_4$  and set the empirical relationship for solubility.

Table D.1: Estimate of the adsorptive capacity of clays in the GISP2 ice core under different adsorptive scenarios for temperature and abundance of CH<sub>4</sub> following Ji et al. (2012). This estimate assumes that all dust in the ice core is composed of clays with a constant composition (Biscaye et al., 1997; Svensson et al., 2000) and abundance given by Ram and Koenig (1997) and Ram et al. (2000). Values are listed as the fraction of potential clay adsorptive capacity, i.e. the ratio of  $n_{xs}^*$  over the adsorptive capacity ( $n_{cap}$ ). Values less than 1 indicate that an estimated adsorptive capacity greater than the observed release/production of  $n_{xs}^*$ . It is important to note that  $n_{xs}^*$  represents only the excess CH<sub>4</sub> released/produced during the ~30 minute second melt-refreeze step of analysis.

$rac{n_{xs}^*}{n_{cap}}$	$T=0^{\circ} C$	$T=30^{\circ} C$
$P_{CH4}=1 \text{ atm}$	0.014	0.021
$P_{CH4}=0.1 \text{ atm}$	0.137	0.215
$P_{CH4}=0.01 \text{ atm}$	1.37	2.15

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