

# **Methane Emission from Ice Sheets – importance for the past, present and future atmosphere (MetICE)**

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**1. Introduction** Recent measurements from the subglacial environment of glaciers in Greenland (1,2) and Iceland (3) show massive release of methane to the atmosphere. This demonstrates that glaciers and ice sheets are active components of the global carbon and methane cycle (4) with potential short- and long term impacts on the global climate system. We lack a reliable estimate of the importance of the total CH<sub>4</sub> emissions from glaciated land areas for the present, the future and the past. The one published estimate on subglacial CH<sub>4</sub> emissions concludes that CH<sub>4</sub> emitted from a glacial meltwater river in Greenland rivals that of major world rivers (1). With very large estimated global carbon reserves in overridden paleosoils (5) or marine sediments (6) below glaciers - which globally surpass the amount stored in non-glaciated permafrost (4) - the recent discoveries of direct CH<sub>4</sub> emissions from glaciers and ice sheets point to an overlooked, but likely significant, emission pathway of CH<sub>4</sub> to the atmosphere.

CH<sub>4</sub> found under glaciers and ice sheets may originate from biological conversion of organic carbon into CH<sub>4</sub> (7) or possibly from low temperature abiotic reactions in the upper part of the Earth's crust (8). Once formed under the ice, the CH<sub>4</sub> may either be stored as dissolved gas in the basal meltwater or accumulate as hydrates under high pressure (i.e. solid CH<sub>4</sub> bound in a crystal structure with water molecules)(6). How long the subglacial CH<sub>4</sub> can be stored under the ice is completely unknown, but is critical to understand to assess the importance of subglacial CH<sub>4</sub> for the past, present and future atmospheric content of CH<sub>4</sub>. The short- and long-term effect of subglacial CH<sub>4</sub> emissions on the atmospheric concentration will depend on the relative rates of net accumulation (production (7) vs oxidation (9)) and subsequent release to the atmosphere. It has been hypothesized that accumulated CH<sub>4</sub> in hydrates (4) below ice sheets can potentially be released rapidly (over centuries) when the ice sheet shrinks, which could lead to massive increases in concentrations of CH<sub>4</sub> in the atmosphere and radiative forcing (6). However, data from ice core air samples covering the last deglaciation indicate that there was not a large release of CH<sub>4</sub> to the atmosphere from hydrate destabilization (10–12). However, the above conclusions are based on reconstructions from ice cores and ice sheet modeling and the measurements proposed in MetICE allow us to directly investigate, in the field, the release mechanism and the likely sources and ages of the released CH<sub>4</sub> from below the Greenland ice sheet using high-resolution field measurements.

**2. Knowledge gap, hypotheses and research framework** Improving the understanding of the processes and the magnitude of CH<sub>4</sub> emissions from the GrIS is required for quantifying the current and potential future contribution of CH<sub>4</sub> from glaciated areas to the natural carbon budget and atmospheric

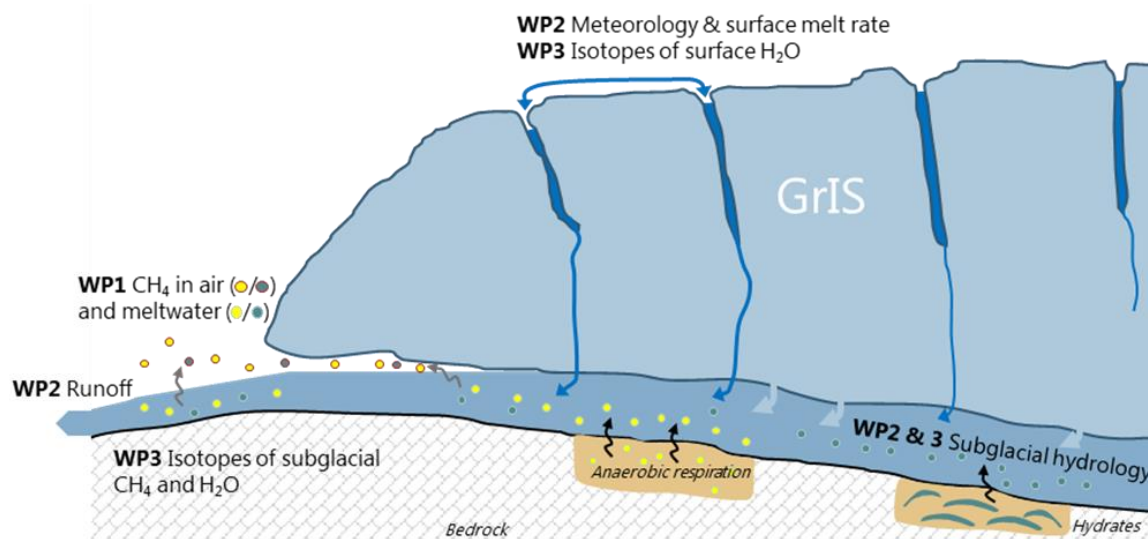
concentration of CH<sub>4</sub>. In MetICE we aim to fill this knowledge gap by investigating the release dynamics of subglacial CH<sub>4</sub> emissions from a meltwater outlet at the Greenland Ice Sheet. What we want to learn about subglacial CH<sub>4</sub> is *the likely source, age and amount of the current emissions* and *dominant process drivers regulating the natural variations in export and emission of subglacial CH<sub>4</sub>*. With this research we can substantiate the role of glaciated areas in the current carbon budget and estimate how periods of glacial retreat or advance may affect the atmospheric mixing ratio of CH<sub>4</sub>.

From the three published studies on the release of subglacial CH<sub>4</sub> to the atmosphere (1–3) it is clear that the discharge of meltwater is the main means of transport of CH<sub>4</sub> from under the ice to the margin of the ice sheet where it is emitted to the atmosphere. Based on our current understanding of the seasonal development of glacial drainage systems and previous ice sheet retreat/advances we formulate the following experimentally testable hypotheses (WP1, WP2 & WP3, Fig. 1):

**Transport hypothesis** (research aim of WP1): The concentration of CH<sub>4</sub> in the meltwater and subglacial air is proportional to the daily variations in meltwater discharge in response to surface melt.

**Mixing hypothesis** (research aim of WP2): The amount of CH<sub>4</sub> emitted is regulated by the connectivity of subglacial sediments to surface melt through subglacial channels and the mixing ratio between basal CH<sub>4</sub> enriched meltwater and supraglacial CH<sub>4</sub> depleted meltwater.

**Source-Age hypothesis** (research aim of WP3): The subglacial CH<sub>4</sub> released from GrIS is biogenic and originates from *in situ* anaerobic respiration of soil organic carbon in subglacial sediments.



**Fig. 1** The research framework of MetICE aims at a full understanding of the subglacial CH<sub>4</sub> emission, turnover, and release in relation to meteorological and glaciological processes in three workpackages (WP). Blue arrows are surface and basal meltwater flows. Black arrows represent the diffusive flux of CH<sub>4</sub> from subglacial sediments or clathrate reservoirs to meltwater. Grey arrows represent evasion of dissolved subglacial CH<sub>4</sub> to the air. The color of circles represent the source of the subglacial CH<sub>4</sub> being either biogenic through methanogenesis (yellow) or from hydrates (dark green). Light green border color of circles signify dissolved CH<sub>4</sub> and red border represents gaseous CH<sub>4</sub>.

**2. State-of-the-art background and preliminary understanding** The vast majority of subglacial meltwater discharge from the GrIS is driven by surface melt at the top of the ice sheet that reaches the base of the ice and is drained to the ice sheet margin via the subglacial channel system (13,14). The interaction time during which subglacial CH<sub>4</sub> of either biological or abiotic origin can dissolve in the meltwater may possibly depend on both the residence time of the meltwater at the CH<sub>4</sub> source and the basal pressure in the dissolution zone. Depending on the distance from the discharge point at the margin to the area under the ice area where the supraglacial meltwater reaches the base of the ice, the meltwater may incorporate CH<sub>4</sub> of different origin at different times over the melt season (Fig. 1). According to our preliminary understanding of the transport dynamics (1), we hypothesize that seasonal variations in subglacial CH<sub>4</sub> concentrations largely follow that of surface melt, but that the total amount of CH<sub>4</sub> being released to the atmosphere could be determined by the CH<sub>4</sub> dissolution from the subglacial CH<sub>4</sub> sources (subglacial sediments or hydrates reservoirs) when these become connected with the subglacial channel system. An improved understanding of both the subglacial hydrology and seasonal development of the subglacial drainage network is essential for linking the total export of CH<sub>4</sub> to the proglacial zone where the emission happens. So far, evasion of CH<sub>4</sub> from the meltwater is the only documented emission pathway of subglacial CH<sub>4</sub> to the atmosphere and there is a strong potential linkage between meltwater discharge and CH<sub>4</sub> emissions (1). Accurate estimates of the total net emission of subglacial CH<sub>4</sub> over time must therefore be based on continuous measurements of both meltwater discharge, CH<sub>4</sub> concentration in the meltwater at different distances to the ice margin and CH<sub>4</sub> concentrations in the air-filled cavities at the contact point between the subglacial domain and the atmosphere (Fig. 1)

Production of subglacial CH<sub>4</sub> may occur from both biological and abiotic processes and these processes can be differentiated by analysis of stable isotopes of carbon (<sup>13</sup>C) and hydrogen (<sup>2</sup>H) in CH<sub>4</sub>. Published studies on subglacial CH<sub>4</sub> so far point to a biogenic source where the CH<sub>4</sub> is likely formed by subglacial methanogenesis, e.g. anoxic decomposition of organic carbon similar to CH<sub>4</sub> produced in wetlands (7,15–18). However, the isotopes of <sup>13</sup>C and <sup>2</sup>H do not convey information on the age of the subglacial CH<sub>4</sub>. To determine the age of the C substrate, analysis of the <sup>14</sup>C content in the subglacial CH<sub>4</sub> can be used for C dating ranging approximately 55.000 years back in time.

In addition to the common stable isotope and radiocarbon characterization of CH<sub>4</sub>, analysis of clumped isotopes of CH<sub>4</sub> (i.e. molecules with more than one rare isotope) have been used to further constrain the processes of CH<sub>4</sub> formation, transport and turnover in different environments. This new field is still in evolution but previous data have proven that clumped isotope measurements allow determining whether a CH<sub>4</sub> sample is in thermodynamic equilibrium or has been affected by kinetic processes(19–21). Thus,

clumped isotope methods provide complementary information to  $^{14/13}\text{C}$  and  $^2\text{H}/\text{H}$  signatures and add an additional isotope dimension for source characterization that may provide unique new information on the methane formation pathways, conditions, and turnover in the subglacial environment.

**3. Study location and work package descriptions** The research framework of MetICE centers on three interlinked experimental work packages (WP1-3), each covering essential activities in both the field at a known  $\text{CH}_4$  source on the southern flank of Isunnguata Sermia glacier in West Greenland and in the laboratory. The proposed study site has been the focus of our recent (2) and past research on glaciology, geochemistry and hydrology (e.g. 15,23) and is ideal for the proposed research as it is easily accessible by car and air through Kangerlussuaq International Airport. Also, meteorological monitoring data for the area is available via PROMICE ([www.promice.dk](http://www.promice.dk)). Thus, the ease of access at the chosen location allows for frequent sampling campaigns to be performed and advanced field equipment to be operated continuously with regular and cost-effective inspections. This significantly adds to the potential for novel discoveries and reduces the risks in the project by minimizing down time of the field based activities.

***WP1 Quantification of subglacial  $\text{CH}_4$  release to the atmosphere via air and meltwater*** (Lead: CJJ (AU), co-lead: JRC (KU) and PhD student)

***WP1.1 Measurements of  $\text{CH}_4$  in subglacial air and meltwater*** A unique feature of the subglacial  $\text{CH}_4$  emissions is that it is likely confined to meltwater outlets point. Here the total emission ( $F_{\text{subglacial}}$ ) can be estimated as the sum of two emission pathways: 1)  $\text{CH}_4$  in the air above the meltwater ( $g\text{CH}_4$ ) at the interface between the ice and the atmosphere and 2)  $\text{CH}_4$  dissolved in the meltwater ( $d\text{CH}_4$ ):

$$F_{\text{subglacial}} = g\text{CH}_4 * \text{subglacial air flow} + d\text{CH}_4 * \text{meltwater discharge rate (eq. 1)}$$

To determine the temporal variation and the total subglacial  $\text{CH}_4$  emission per unit time over the melt season, we will develop and deploy an automated measurement system that simultaneously and at a high sampling frequency can measure both the  $g\text{CH}_4$  and  $d\text{CH}_4$  at the outlet of the glacier. This system will be based on low power metal oxide sensors for  $\text{CH}_4$  that are regularly calibrated in the field with a high precision laser spectroscopy analyzer for  $\text{CH}_4$  (2). These data together with the meltwater discharge and airflow measurements (WP2) are used to estimate the total subglacial  $\text{CH}_4$  emission (equation 1).

***WP1.2 Sampling of subglacial and surface meltwater and gas for isotope and geochemistry*** The continuous measurements of  $g\text{CH}_4$  and  $d\text{CH}_4$  will be supplemented with discrete gas and water samples in campaigns prior to and in the early, maximum and decreasing stages of the melt season. These samples will be used in WP3 for determination the isotopic composition of the meltwater itself and  $g\text{CH}_4$  and  $d\text{CH}_4$  as well as the  $^{14}\text{C}$  and clumped isotope signatures of  $g\text{CH}_4$ . Basic geochemistry, such as pH, alkalinity and elemental composition of the meltwater will also be determined.

*Major outcomes of WP1 are the unique and novel data of the magnitude and seasonal variations of subglacial CH<sub>4</sub> emission and essential gas and water samples for downstream analysis in WP3.*

**WP2 Meteorology and glacial hydrology** (Lead: JRC (KU), co-lead: CJJ (AU) and PhD student)

WP2.1 Continuous measurement of meltwater discharge and subglacial air flow A station for continuous measurements of meltwater discharge from the hydrological catchment area will be established at the outlet to determine the temporal variations in discharge across the melt season. A relation between runoff, water level and cross-sectional area of the river (QH curve) is determined in field season 1 by regular dye (rhodamin) tracer calibration (23). The QH curve is used for field seasons 2 & 3 to estimate the meltwater discharge, At the outlet point, wind speed sensors will be installed to continuously measure the flow rate of meltwater driven air flow (2). Collectively, these measurements are used in the calculation of the total export of dCH<sub>4</sub> and gCH<sub>4</sub> from the ice catchment area of that outlet (eq. 1).

WP2.2 Comparative analysis of measured meltwater discharge and surface melt data: Monitoring data of meteorological variables needed to determine the melt rates at the surface of the GrIS in the study location's ice catchment is publically available at [www.promice.dk](http://www.promice.dk). To access and interpret these data we will involve Andreas Ahlstrøm (GEUS, Denmark). The surface melt rates, together with the meltwater discharge rates (WP2.1), are used to estimate the contribution of subglacial and surface melt to the total runoff (Fig. 1) across the melt season. This will provide important information on the development of the subglacial drainage system, which can explain the patterns in observed export and emission of subglacial CH<sub>4</sub> (WP1) and its isotope geochemistry (WP3).

*The major outcome of WP2 is the time series of surface melt and total discharge that form the basis for calculation of the total CH<sub>4</sub> emission (WP1) as well as connecting the insight from the temporal variation of the CH<sub>4</sub> concentrations (WP1) to the isotopic composition of CH<sub>4</sub> and meltwater (WP3).*

**WP3 Isotope geochemistry of dissolved CH<sub>4</sub> in subglacial water and air** (Lead: TB (KU), co-lead: TR (UU), JRC (KU), post-doc)

WP3.1 Stable isotope analysis of <sup>18</sup>O and <sup>2</sup>H in meltwater: Provided the isotopic composition of surface and bottom ice differs substantially, which we expect, repeated seasonal measurements of δ<sup>18</sup>O and δD in meltwater can reveal the degree of mixing between subglacial and supraglacial melt water (*Mixing hypothesis*). As the melt season progresses and the glacial drainage system develops, the isotopic composition of meltwater becomes dominated by surface water (13). By linking the seasonal variations in δ<sup>18</sup>O and δ<sup>2</sup>H to rates of surface melt and meltwater discharge (WP2) we will obtain direct measurements of both the source and degree of mixing of the meltwater, which will provide a robust indicator of the source area of the CH<sub>4</sub> being emitted (WP1).

WP3.2 Stable isotope analyses of  $^{13}\text{C}$  and  $^2\text{H}$  in  $\text{CH}_4$ : The “Keeling plot” approach is a proven method to determine the isotope composition of unknown sources of  $\text{CH}_4$  in situations where methane from one source is added to a constant background (24). For more complex systems, mixing, and oxidation signature need to be taken into account. For testing the *mixing* and *source-age* hypotheses of MetICE, we will apply this method to analyze how changes in the variations in stable isotopes of the subglacial  $\text{CH}_4$  over time can be linked to the processes of known  $\text{CH}_4$  isotope discrimination and thereby the likely  $\text{CH}_4$  reservoirs under the ice. Repeated sampling and analysis  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  will reveal if changes in  $\text{CH}_4$  sources occur as the subglacial drainage system evolves over the melt season and will allow an assessment of the degree of oxidation of subglacial  $\text{CH}_4$  (9). We will collect gas and water samples at three mixing levels (distances from the margin of the GrIS) between the atmospheric background and subglacial  $\text{CH}_4$  and interpret the covariations of  $\text{CH}_4$  concentration and isotopic composition.

WP3.3 Clumped isotopic composition and  $^{14}\text{C}$ -age of  $\text{CH}_4$ : The clumped isotope signatures of  $\text{CH}_4$  refer to the deviation of the abundance of  $\text{CH}_4$  molecules with two heavy isotopes (e.g.  $^{13}\text{C}$ -D or D-D methane) relative to the abundance that is statistically expected from their bulk ( $^{13}\text{C}$  and D) isotopic composition. In thermodynamic equilibrium, clumped isotope signatures are a function of temperature only and can thus be used as (paleo) thermometers (19–21,25). However, it has clearly been demonstrated that kinetic effects lead to large and significant deviations from these theoretically expected values. Thus, the clumped isotope measurements, together with the traditional signatures, will allow an assessment whether the sub-glacial  $\text{CH}_4$  is in thermodynamic equilibrium, if so at which temperature, and if not, which other processes may have affected it. Age determination of the subglacial  $\text{CH}_4$  is achieved by analyzing the amount of  $^{14}\text{C}$  present in the subglacial  $\text{CH}_4$ . Together with the analysis of stable isotopes, the  $^{14}\text{C}$  dates will provide clear indications on whether the subglacial  $\text{CH}_4$  emissions is part of a shorter or longer carbon cycle and thereby determine its overall long-term role in the natural global climate system (*Source-age hypothesis*). The clumped isotopes are measured at IMAU and  $^{14}\text{C}$  are prepared by IMAU and measured in Bern (Prof. Dr. Sönke Szidat). In MetICE we will be the first international first team applies these emerging and instrumentally very challenging fields of research to subglacial  $\text{CH}_4$ .

*The major outcome of WP3 is the first ever, complete dataset characterizing the isotopic composition and age of subglacial  $\text{CH}_4$  emitted to the atmosphere and its relation to sources of meltwater.*

**5. Work plan, project organization and research training** During the project period (Table 1) we propose to conduct the field measurement program (WP1 & WP2) for three consecutive field seasons, including short winter campaigns (Table 1). This will allow us to make more robust testing of the hypotheses in MetICE by including potentially large inter annual variations in surface melt and discharge.

In 2021 the research infrastructure on site in Greenland is established and sampling and laboratory protocols for isotopic composition of air and water developed (Table 1). Hence, we can mitigate risks of the subsequent field and laboratory work during and after field seasons 2 & 3. MetICE will seek out logistic support in Kangerlussuaq from the EASTGRIP project (TB is member) which facilitates transport of field equipment and samples to and from Greenland.

**Table 1 Timeline of WP1 – 3 in the period January 2021 to June 2024 including major milestones (M) (M1 – M6).**

	Year	2021 Field season 1				2022 Field season 2				2023 Field season 3				2024	
		Month: 1-3	4-6	7-9	10-12	1-3	4-6	7-9	10-12	1-3	4-6	7-9	10-12	1-3	4-6
Project Management		X M1				X				X				X	
WP1	WP1.1 Continuous CH <sub>4</sub> in water and air	[shaded box]				[shaded box]				[shaded box]				[shaded box]	
	WP1.2 Discrete air and water samples	[shaded box]				[shaded box]				[shaded box]				[shaded box]	
WP2	WP2.1 Glacial hydrology	[shaded box]				[shaded box]				[shaded box]				[shaded box]	
	WP2.2 Meteorology	[shaded box]				[shaded box]				[shaded box]				[shaded box]	
WP3	WP3.1 - 3.3 Isotopes of CH <sub>4</sub> and H <sub>2</sub> O	[shaded box]				[shaded box]				[shaded box]				[shaded box]	
Publication & Outreach						[shaded box]								[shaded box]	

MetICE is organized around; Jesper R. Christiansen (JRC) (PI, University of Copenhagen (KU)), Christian J. Jørgensen (CJJ) (Aarhus University (AU)), Thomas Blunier (TB) (KU) and Thomas Röckmann (TR) (Utrecht University (UU), Netherlands). At KU, Vasileios Gkinis assist in analyses of water and CH<sub>4</sub> isotopes and at UU Carina van der Veen and Maria Elena Popa assist with clumped isotope and preparation of <sup>14</sup>C analyses. JRC works with subglacial CH<sub>4</sub> (2) and CJJ is designing low cost trace gas analyzers for field applications. TB is leading an isotope laboratory for ice, gas and water samples. TR is leading one of the few laboratories doing clumped isotopes. All four have participated in field campaigns in the Arctic and have experience with equipment for gas and water sampling.

Regular meetings and annual gatherings (X in table 1) will ensure progress. Project management is guided by six milestones (M). M1: hiring of PhD student and plan for hiring post doc in 2021. M2: establishment of field monitoring station in Greenland and tested sampling protocol for air and water. M3: finalization of testing of laboratory methods for CH<sub>4</sub> and H<sub>2</sub>O isotopes at KU and UU. M4: successful collection of field data for two melt seasons. M5: isotope analysis finalized. M6: project finalization by manuscript submission/publication and PhD defence. Dissemination of the project results will be at international conferences, peer-reviewed papers and popular science articles.

Research training of the PhD is in WP1/2 and the post-doc in WP3. The PhD and post-doc will be members of the research groups of JRC/TB at KU, respectively. The PhD is enrolled in the PhD School at SCIENCE (KU) and JRC is the main supervisor and CJJ co-supervisor. TB is the main point of contact for the post doc. The PhD and post-doc have access to office space, computer, laboratory facilities and technical and HR support. Career development is possible through courses in project management and leadership offered by SCIENCE.

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