Zheng, Y., Fang, Z., Fan, T., Liu, Z., Wang, Z., Li, Q., ... Naafs, B. D. A. (2019). Operation of the boreal peatland methane cycle across the past 16 k.y. *Geology, 48*(1), 82-86. https://doi.org/10.1130/G46709.1
Operation of the boreal peatland methane cycle across the past 16 k.y.

Yanhong Zheng¹, Zhengkun Fang¹, Tongyu Fan¹, Zhao Liu², Zhangzhang Wang¹, Qiuyan Li¹, Richard D. Pancost³ and B. David A. Naafs⁴*
¹State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi’an, 710069, P.R. China
²School of Environmental & Chemical Engineering, Xi’an Polytechnic University, Xi’an, 710048, P.R. China
³Organic Geochemistry Unit, School of Earth Sciences, School of Chemistry, Cabot Institute for the Environment, University of Bristol, Bristol BS8 1TS, UK

ABSTRACT

The role of boreal wetlands in driving variations in atmospheric methane (CH₄) concentrations across the last deglaciation (20–10 ka) and the Holocene is debated. Most studies infer the sources of atmospheric methane via ice-core records of methane concentration and its light stable isotopic composition. However, direct evidence for variations in the methane cycle from the wetlands themselves is relatively limited. Here, we used a suite of biomarker proxies to reconstruct the methane cycle in the Chinese Hani peat across the past 16 k.y. We found two periods of enhanced methanogenesis, at ca. 15–11 ka and ca. 10–6 ka, whereas weak methanogenesis characterized the late Holocene. These periods of enhanced methanogenesis relate to periods of high/increasing temperatures, supporting a temperature control on the wetland methane cycle. We found no biomarker evidence for intense methanotrophy throughout the past 16 k.y., and, contrary to previous studies, we found no clear control of hydrology on the peatland methane cycle. Although the onset of methanogenesis at Hani at ca. 15 ka coincided with a negative shift in methane δ¹³C in the ice cores, there is no consistent correlation between changes in the reconstructed methane cycle of the boreal Hani peat and atmospheric CH₄ concentrations.

INTRODUCTION

Methane is an important gas for atmospheric chemistry because it accounts for ~20% of the total radiative forcing from all of the long-lived and globally mixed greenhouse gases. Atmospheric methane concentrations obtained from ice cores demonstrate that across the last deglaciation (between 20 and 10 ka), concentrations doubled from ~350 to 700 ppbv (Stauffer et al., 1988). They then exponentially increased to >1850 ppbv during the past ~150 yr.

However, the source of the atmospheric methane increase across the last deglaciation remains intensely debated (Chappellaz et al., 1990, 1993; Kennett et al., 2000; Bock et al., 2017; Petrenko et al., 2017; Treat et al., 2019), highlighting a fundamental gap in our understanding of the methane cycle and Earth’s climate system. The main hypothesis to explain the deglacial increase revolves around wetlands, the dominant natural source of methane (Saunois et al., 2019). According to this hypothesis, an expansion of boreal wetlands as the continental ice sheets retreated, together with an intensified methane cycle within boreal and tropical wetlands in response to higher terrestrial temperatures, led to the observed increase in atmospheric methane (Chappellaz et al., 1990). Reconstructing past changes in the spatial extent of wetlands has been the focus of many studies (Chappellaz et al., 1993; Loisel et al., 2017; Treat et al., 2019), but the evolution of the methane cycle within wetlands across the last deglaciation is virtually unconstrained. Here, we addressed this critical gap in paleoclimate research by using a state-of-the-art biomarker approach to reconstruct the wetland methane cycle across the past 16 k.y.

METHODS

The boreal Hani peat deposit (42°13’N, 126°31’E; Fig. 1) is situated in Liuhe County in Jilin Province, China, at an elevation of 910 m on the western flank of the Changbai Mountains. The Hani peat is characterized by minerotrophic and meso- to oligotrophic conditions. The vegetation predominantly consists of sedges (e.g., Carex, Cyperaceae, and Rhynchospora) and Sphagnum. The core we collected from the Hani peat deposit consists of 574 cm of brown to dark-brown peat, underlain by 11 cm of brown peat with sand (age ca.10.4 ka; Fig. 2), and then 262 cm of dark-brown peat. Below 847 cm depth, the sediment is grayish-green mud, representing the original lacustrine depositional conditions (for details, see Zheng et al., 2017). Chronostratigraphy of the core is based on 10 accelerator mass spectrometry ¹⁴C dates from plant fragments in peat intervals and bulk organic matter in the bottom lacustrine layer (Fig. 2). The procedures for lipid extraction and analysis have been described elsewhere (Zheng et al., 2017).

Here, we focused on reconstructing the abundance of methanogens that produce methane, and methanotrophs that consume methane, in peat. Ultimately, it is the balance between these two communities that controls the amount of methane that escapes into the atmosphere. We explored the hypothesis that more methane was emitted from boreal wetlands due to an intensified methane cycle across the last deglaciation and the Holocene. Our down-core records might have a small temporal offset because aerobic oxidation of methane by bacterial methanotrophs occurs in the acrotelm (peat containing living plants), while methanogenesis by Archaea occurs at depth in the catotelm (peat containing dead plant material). We cannot quantify this offset or whether it has been constant through the past 16 k.y.

Although biomarker concentrations in natural samples can be influenced by multiple processes and do not always correlate with...
We used archaeol and isoGDGT-0 accumulation rates to infer variability in the methanogen community over time. Over the last deglaciation and the Holocene, changes in this archaeal biomarker content were broadly associated with changes in bacterial branched GDGT-based estimates of mean annual air temperature (MAAT; Zheng et al., 2017) and mean high-latitude summer insolation (Fig. 2). Overall, strong (weak) methanogenesis corresponds to high (low) temperatures and high (low) summer insolation. For example, the Holocene climatic optimum is associated with a period of high archaeal and isoGDGT-0 accumulation, suggesting enhanced methanogenesis. During the late Holocene (starting at ca. 6 ka), temperatures and mean summer insolation declined in tandem with a decline in methanogenesis. Numerous studies have indicated that methanogenesis has a strong dependence on temperature, with warmer conditions being associated with greater methanogenesis and CH₄ production in wetlands (van Winden et al., 2012a; Yvon-Durocher et al., 2014). Our Hani peat record extends these findings and shows that changes in temperature also drive changes in boreal wetland methanogenesis on millennial time scales.

Diploptene δ¹³C values in Hani peat were relatively enriched, especially during the period between 8 and 6 ka (up to ~30‰), indicating a mixed input of heterotrophic and methanotrophic bacteria. These δ¹³C values do not exclude the presence of an active methanotrophic community (van Winden et al., 2010) and are similar to those observed in a recent global survey of modern peatlands (Inglis et al., 2019). However, they are more enriched compared to those in other Chinese peatlands, where values as low as ~50‰ have been measured during the Holocene (van Winden et al., 2012a; Yvon-Durocher et al., 2014). This suggests a less-active methanotrophic community at Hani compared to that seen elsewhere in China.
The overall high and invariable C33n-alkane δ13C values indicate that, at Hani, higher plants did not significantly assimilate substantial amounts of isotopically depleted methane across the last deglaciation nor during the Holocene. Assuming that the C33n-alkane δ13C values are representative for the peat plant material, and hence organic substrate, their relative stability further suggests that the minor variations in diploptene δ13C values reflect changes in microbial processes rather than a change in organic matter substrate. The lower diploptene δ13C values in the early and late Holocene could reflect minor increases in methanotrophy. Alternatively, or in addition to temperature, at Hani the Holocene was also characterized by variations in hydrology, shifting from dry conditions during the early Holocene to a wet late Holocene (Zheng et al., 2018). These can drive changes in methanogenesis. In fact, other peatlands in China do document large changes in methanogenesis (Zheng et al., 2014; Huang et al., 2018) and methanotrophy (Zheng et al., 2017), together with 14C dates (gray triangles). The onset of peat formation, archaeal methanogenesis (increase in isoGDGT-0 and archaeol accumulation rates), and an increase in bacterial community size (increase in diploptene abundance) at Hani at ca. 15.4 ka coincide with a shift in methane δ13C values in Antarctic ice cores (Möller et al., 2013; Bock et al., 2017). This lends support to the theory that the development of boreal wetlands across the high northern latitudes during the last deglaciation played a role in driving the global atmospheric methane δ13C budget. However, our methanogen and methanotroph proxies exhibited no relationship...
with atmospheric methane concentrations. During the rapid increase in atmospheric methane concentrations that started at ca. 14 ka, there is no significant change in methanogenesis or methanotrophy recorded in our biomarker proxies at Hani. Similarly, the return to low methane concentrations during the Younger Dryas is not matched by a change in the Hani methane cycle, and the late Holocene gradual increase in atmospheric methane concentrations coincides with a decline in methanogenesis at Hani.

Methane cycling at Hani, especially the indicators for methanogenesis, instead appears to correspond to local climatic factors. This is expected, and it allows an examination of how methane cycling in boreal wetlands changed more generally during the Holocene. Globally, boreal wetlands experienced an increase in mean summer insolation, and hence temperature, during the early Holocene (maximum insolation at ca. 10–8 ka; Fig. 2), followed by a decline during the late Holocene. Therefore, a decline in the intensity of the methane cycle within boreal peatlands seems an unlikely reason for the decline in atmospheric methane concentrations from 10 to 6 ka, when temperatures were at a Holocene maximum. The same holds true for the observed increase in atmospheric methane concentrations during the past 6 k.y., when mean summer insolation and temperature declined (Zheng et al., 2017). A minor role for changes in the methane cycle within boreal peatlands is further supported by the spatially variable change in peatland hydrology across the Boreal realm during the Holocene (Borgmark and Wastegård, 2008; Zheng et al., 2018), and the heterogeneous influence this exerted on the peatland methane cycle. It is more likely that most of the changes in atmospheric methane concentration during the Holocene were driven by changes in the (spatial) extent of wetlands and not by changes in intensity of the methane cycle in peatlands themselves.

CONCLUSIONS
Here, we used biomarker accumulation rates and compound-specific δ13C values to explore changes in the methane cycle at the Hani peatland across the past 16 k.y. The δ13C values and abundance of diploptene at Hani provide no evidence for significant variations in methanotrophy across the past 16 k.y. Instead, they suggest a less-dominant methanotrophic community than observed elsewhere in Chinese Holocene peatlands. On the other hand, archaeal biomarkers indicative for the methanogenic community (archaeol and isoGDGT-0) show that methanogenesis did fluctuate and was particularly enhanced during periods of increasing temperature, such as the last deglaciation and the Holocene climatic optimum. Although the onset of methanogenesis, as indicated by a sharp increase in concentration of archaeal biomarkers, coincided with a negative shift in δ13Cmethane in Antarctic ice cores, there is no consistent relationship between changes in archaeal biomarkers, and hence methanogenesis, at the boreal Hani peat and atmospheric CH4 concentrations. If Hani is representative for boreal wetlands globally, our biomarker results imply that boreal wetlands were not dominant in driving atmospheric CH4 concentrations across the last deglaciation and the Holocene. This hypothesis needs further testing across a range of boreal wetlands, and future work should also focus on the methane cycle within tropical peatlands to explore how this evolved across the last deglaciation and the Holocene.

ACKNOWLEDGMENTS
We thank the Natural Environment Research Council (UK) for partial funding of the mass spectrometry facilities at the University of Bristol (contract no. R8/ H1/063; www.lsmsf.co.uk). This work was supported by the National Natural Science Foundation of China (grants 41872031 and 41372033), the Outstanding Young Scientist Foundation of Shaanxi Province (grant 2018JC-021), a Marie Curie International Incoming Fellowship within the 7th European Community Framework Programme, funds from the Laboratory of Loess and Quaternary Geology (grant SKLQGG1731), and the MOST Special Fund from the State Key Laboratory of Continental Dynamics, Northwest University, Xi’an, China. Pancost and Naafs were funded through the advanced European Research Council grant “the Greenhouse Earth System” (T-GRES, project reference 345023). Naafs also received additional support through a Royal Society Tata University research fellowship. We thank two anonymous reviewers for their constructive comments.

REFERENCES CITED
Basiliko, N., Yavitt, J.B., Dees, P.M., and Merkel, S.M., 2003, Methane biogeochemistry and methanogenic communities in two northern peatland ecosystems, New York State: Geomicrobiology Journal, v. 20, p. 563–577, https://doi.org/10.1080/13811165.
Bock, M., Schmitt, J., Beck, J., Seth, B., Chappellaz, J., and Fischer, H., 2017, Glacial/interglacial wetland, biomass burning, and geologic methane emissions constrained by dual stable isotopic CH4 ice core records: Proceedings of the National Academy of Sciences of the United States of America, v. 114, p. E5778–E5786, https://doi.org/10.1073/pnas.1613833114.
Borgmark, A., and Wastegård, S., 2008, Regional and local patterns of peat humification in three raised peat bogs in Sweden: Geoforum, v. 39, p. 176–187, https://doi.org/10.1016/j.geoforum.2008.10.001.
Chappellaz, J., Barnola, J.M., Raynaud, D., Korotkevich, Y.S., and Lorius, C., 1990, Ice-core record of atmospheric methane over the past 160,000 years: Nature, v. 345, p. 127–131, https://doi.org/10.1038/345127a0.
Chappellaz, J.A., Fung, I.Y., and Thompson, A.M., 2000, Carbon isotopic evidence for methane hydrate instability during Quaternary interstadials: Science, v. 288, p. 128–133, https://doi.org/10.1126/science.288.5463.128.
Koga, Y., Nishihara, M., Morii, H., and Akagawa-Matsushita, M., 1993, Either polar lipids of methanogenic bacteria: Structures, comparative aspects, and biosyntheses: Microbiology and Molecular Biology Reviews, v. 57, p. 164–182.
Liu, Y., and Whitman, W.B., 2008, Metabolic, phylogenetic, and ecological diversity of the methanogenic Archaea: Annals of the New York Academy of Sciences, v. 1125, p. 171–189, https://doi.org/10.1196/annals.1419.019.
Loisel, J., et al., 2017, Insights and issues with estimating northern peatland carbon stocks and fluxes since the Last Glacial Maximum: Earth-Science Reviews, v. 165, p. 55–80, https://doi.org/10.1016/j.earscirev.2016.12.001.
Müller, L., Sowers, T., Bock, M., Spahn, R., Behrens, M., Schmitt, J., Miller, H., and Fischer, H., 2013, Independent variations of CH4 emissions and isotopic composition over the past 160,000 years: Nature Geoscience, v. 6, p. 885–890, https://doi.org/10.1038/NGEO1928.
Naafs, B.D.A., Inglis, G.N., Blewett, J., McClymont, E.L., Lauritano, V., Xie, S., Evershed, R.P., and Pancost, R.D., 2019, The potential of biomarker proxies to trace climate, vegetation, and biogeochemical processes in peat: A review: Global and Planetary Change, v. 179, p. 57–79, https://doi.org/10.1016/j.gloplacha.2019.05.006.
Pancost, R.D., and Simming, Danjost, J.S., 2003, Carbon isotopic compositions of prokaryotic lipids as tracers of carbon cycling in diverse ecosystems: Chemical Geology, v. 195, p. 29–58, https://doi.org/10.1016/j.chemgeo.2003.02.0387-X.
Pancost, R.D., et al., 2011, Archaeal as a methanogen biomarker in ombrotrophic bogs: Organic Geochemistry, v. 42, p. 1293–1297, https://doi.org/10.1016/j.orggeochem.2011.07.003.
Petrenko, V.V., Smith, A.M., Schaefer, H., Riedel, K., Brook, E., Baggenstos, D., Harth, C., Hua, Q., et al., 2017, Minimal geological methane emissions during the Younger Dryas—Preboreal abrupt warming event: Nature, v. 548, p. 443–446, https://doi.org/10.1038/nature23116.
Sannois, M., Stavert, A.R., Poulet, B., Bousquet, P., Canadell, J.G., Jackson, R.B., Raymond, P.A., Dlugokencky, E.J., et al., 2019, The global methane budget 2000–2017: Earth System Science Data Discussion, v. 2019, p. 1–138, https://doi.org/10.5194/ds-2019-128.
Schlitzer, R., 2018, Ocean Data View: http://odv.awi.de (accessed January 2019).
Segarra, K.E.A., Schubotz, F., Samarkin, V., Yoshinaga, M.Y., Hinrichs, K.U., and Joyce, S.B., 2015, High rates of anaerobic methane oxidation in freshwater wetlands reduce potential atmospheric methane emissions: Nature Communications, v. 6, p. 7477, https://doi.org/10.1038/ncomms8477.
Stauffer, B., Lochbrunner, E., Oescher, H., and Schwander, J., 1988, Methane concentration in the glacial atmosphere was only half that of the preindustrial Holocene: Nature, v. 332, p. 812–814, https://doi.org/10.1038/332812a0.
Sunamura, M., Koga, Y., and Ohwada, K., 1999, Biomass measurement of methanogens in the sediments of Tokyo Bay using archaeal lipids:
Treat, C.C., Kleinen, T., Broothaerts, N., Dalton, A.S., Dommann, R., Douglas, T.A., Drexler, J.Z., Finkelstein, S.A., et al., 2019. Widespread global peatland establishment and persistence over the last 130,000 years: Proceedings of the National Academy of Sciences of the United States of America, v. 116, p. 4822–4827, https://doi.org/10.1073/pnas.1813305116.

Urbanová, Z., and Bárta, J., 2014, Microbial community composition and in silico predicted metabolic potential reflect biogeochemical gradients between distinct peatland types: FEMS Microbiology Ecology, v. 90, p. 633–646, https://doi.org/10.1111/1574-6941.12422.

van Winden, J.F., Kip, N., Reichart, G.-J., Jetten, M.S.M., Op den Camp, H.J.M., and Sinninghe Damsté, J.S., 2010, Lipids of symbiotic methane-oxidizing bacteria in peat moss studied using stable carbon isotopic labelling: Organic Geochemistry, v. 41, p. 1040–1044, https://doi.org/10.1016/j.orggeochem.2010.04.015.

van Winden, J.F., Rechard, G.-J., McNamara, N.P., Ben-thien, A., and Damsté, J.S.S., 2012a, Temperature-induced increase in methane release from peat bogs: A mesocosm experiment: PLoS One, v. 7, p. e39614, https://doi.org/10.1371/journal.pone.0039614.

van Winden, J.F., Talbot, H.M., Kip, N., Reichart, G.-J., Pol, A., McNamara, N.P., Jetten, M.S.M., Op den Camp, H.J.M., et al., 2012b, Bacterio-hopanepolyol signatures as markers for methanotrophic bacteria in peat moss: Geoichimica et Cosmochimica Acta, v. 77, p. 52–61, https://doi.org/10.1016/j.gca.2011.10.026.

Yvon-Durocher, G., Allen, A.P., Bastviken, D., Conrad, R., Gudasz, C., St-Pierre, A., Thanh-Duc, N., and del Giorgio, P.A., 2014, Methane fluxes show consistent temperature dependence across microbial to ecosystem scales: Nature, v. 507, p. 488–491, https://doi.org/10.1038/nature13164.

Zheng, Y., Singarayer, J.S., Cheng, P., Yu, X., Liu, Z., Valdes, P.J., and Pancost, R.D., 2014, Holocene variations in peatland methane cycling associated with the Asian summer monsoon system: Nature Communications, v. 5, p. 4631, https://doi.org/10.1038/ncomms5631.

Zheng, Y., Pancost, R.D., Liu, X., Wang, Z., Naafs, B.D.A., Xie, X., Liu, Z., Yu, X., et al., 2017, Atmospheric connections with the North Atlantic enhanced the deglacial warming in northeast China: Geology, v. 45, p. 1031–1034, https://doi.org/10.1130/G39401.1.

Zheng, Y., Pancost, R.D., Naafs, B.D.A., Li, Q., Liu, Z., and Yang, H., 2018, Transition from a warm and dry to a cold and wet climate in NE China across the Holocene: Earth and Planetary Science Letters, v. 493, p. 36–46, https://doi.org/10.1016/j.epsl.2018.04.019.

Printed in USA