

# Changes in peat chemistry associated with permafrost thaw increase greenhouse gas production

Suzanne B. Hodgkins<sup>a,1</sup>, Malak M. Tfaily<sup>a</sup>, Carmody K. McCalley<sup>b</sup>, Tyler A. Logan<sup>c</sup>, Patrick M. Crill<sup>d</sup>, Scott R. Saleska<sup>b</sup>, Virginia I. Rich<sup>e</sup>, and Jeffrey P. Chanton<sup>a,1</sup>

<sup>a</sup>Department of Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, FL 32306; <sup>b</sup>Department of Ecology and Evolutionary Biology, University of Arizona, Tucson, AZ 85721; <sup>c</sup>Abisko Scientific Research Station, Swedish Polar Research Secretariat, SE-981 07 Abisko, Sweden; <sup>d</sup>Department of Geological Sciences, Stockholm University, SE-106 91 Stockholm, Sweden; and <sup>e</sup>Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ 85721

Edited by Nigel Roulet, McGill University, Montreal, Canada, and accepted by the Editorial Board March 7, 2014 (received for review August 1, 2013)

Carbon release due to permafrost thaw represents a potentially major positive climate change feedback. The magnitude of carbon loss and the proportion lost as methane (CH<sub>4</sub>) vs. carbon dioxide (CO<sub>2</sub>) depend on factors including temperature, mobilization of previously frozen carbon, hydrology, and changes in organic matter chemistry associated with environmental responses to thaw. While the first three of these effects are relatively well understood, the effect of organic matter chemistry remains largely unstudied. To address this gap, we examined the biogeochemistry of peat and dissolved organic matter (DOM) along a ~40-y permafrost thaw progression from recently- to fully thawed sites in Storölen Mire (68.35°N, 19.05°E), a thawing peat plateau in northern Sweden. Thaw-induced subsidence and the resulting inundation along this progression led to succession in vegetation types accompanied by an evolution in organic matter chemistry. Peat C/N ratios decreased whereas humification rates increased, and DOM shifted toward lower molecular weight compounds with lower aromaticity, lower organic oxygen content, and more abundant microbially produced compounds. Corresponding changes in decomposition along this gradient included increasing CH<sub>4</sub> and CO<sub>2</sub> production potentials, higher relative CH<sub>4</sub>/CO<sub>2</sub> ratios, and a shift in CH<sub>4</sub> production pathway from CO<sub>2</sub> reduction to acetate cleavage. These results imply that subsidence and thermokarst-associated increases in organic matter lability cause shifts in biogeochemical processes toward faster decomposition with an increasing proportion of carbon released as CH<sub>4</sub>. This impact of permafrost thaw on organic matter chemistry could intensify the predicted climate feedbacks of increasing temperatures, permafrost carbon mobilization, and hydrologic changes.

High-latitude soils in the Northern Hemisphere contain an estimated 1,400–1,850 petagrams (Pg) of carbon, of which ~277 Pg is in peatlands within the permafrost zone (1, 2). This quantity of 277 Pg represents over one-third of the carbon stock in the atmosphere (*ca.* 800 Pg) (3). The fate of this carbon in a warming climate—i.e., the responses of net carbon balance and CH<sub>4</sub> emissions—is important in predicting climate feedbacks of permafrost thaw. Although northern peatlands are currently a net carbon sink, and have been since the end of the last glaciation, they are a net source of CH<sub>4</sub> (4, 5), emitting 0.046–0.09 Pg of carbon as CH<sub>4</sub> per year (4, 6, 7). Due to CH<sub>4</sub>'s disproportionate global warming potential (33× CO<sub>2</sub> for 1 kg CH<sub>4</sub> vs. 1 kg CO<sub>2</sub> at a 100-y timescale) (8), this is equivalent to 6–12% of annual fossil fuel emissions of CO<sub>2</sub> (8.7 Pg of C) (9). The thaw of permafrost peatlands may alter their CH<sub>4</sub> and CO<sub>2</sub> emissions due to mobilization of formerly frozen carbon, higher temperatures, altered redox conditions, and evolving organic matter chemistry. Changes in carbon emissions, and in CH<sub>4</sub> emission in particular, could have potentially significant climate impacts.

CH<sub>4</sub> is produced by two primary mechanisms (10–12), distinguishable by  $\delta^{13}\text{C}$  values. The reduction of CO<sub>2</sub> with H<sub>2</sub> (hydrogenotrophic production) generally produces CH<sub>4</sub> more depleted in  $^{13}\text{C}$  ( $\delta^{13}\text{C} = -110$  to  $-60\text{‰}$ ) than CH<sub>4</sub> produced by the cleavage of acetate into CH<sub>4</sub> and CO<sub>2</sub> ( $\delta^{13}\text{C} = -70$  to  $-30\text{‰}$ ) (10, 11, 13–15). Due to the coproduction or utilization of CO<sub>2</sub>

during CH<sub>4</sub> production (10–12, 16, 17),  $\delta^{13}\text{C}_{\text{CH}_4}$  also depends on  $\delta^{13}\text{C}_{\text{CO}_2}$ , so we use the more robust parameter  $\alpha_{\text{C}}$  (10) to represent the isotopic separation between CH<sub>4</sub> and CO<sub>2</sub>. Despite the two production pathways' stoichiometric equivalence (17), they are governed by different environmental controls (18). Distinguishing these controls and further mapping them is therefore essential for predicting future changes in CH<sub>4</sub> formation under changing environmental conditions. Several studies have suggested that the proportion of CH<sub>4</sub> produced by acetate cleavage relative to CO<sub>2</sub> reduction is likely to increase with increasing pH (19, 20) and organic matter reactivity (12, 14, 15), but direct evidence of the latter is lacking.

In this study, we tested the hypotheses that (i) organic matter reactivity increases with permafrost thaw due to thaw-induced subsidence and associated shifts in hydrology and plant community (21), and (ii) CH<sub>4</sub> production shifts from hydrogenotrophic to acetoclastic due to this increase in organic matter reactivity. We assessed organic matter reactivity along a distinct chronosequence of permafrost thaw stages with differing plant community and hydrology by performing anaerobic incubations of peat collected along this sequence. We then compared the results to peat and dissolved organic matter (DOM) chemical structure, as described by C/N ratios and Fourier transform infrared (FTIR) spectroscopy of peat and Fourier transform ion cyclotron resonance mass spectrometry

## Significance

We address the effect of thawing permafrost, and attendant subsidence-induced shifts in hydrology and plant community structure, on CH<sub>4</sub> and CO<sub>2</sub> production potentials and mechanisms driven by changes in organic matter chemical composition in a thawing peatland complex. Advanced analytical characterization of peat and dissolved organic matter along the thaw progression indicated increasingly reduced organic matter experiencing greater humification rates, which were associated with higher relative CH<sub>4</sub> and CO<sub>2</sub> production potentials, increasing relative CH<sub>4</sub>/CO<sub>2</sub> production ratios, and shifts from hydrogenotrophic to acetoclastic methanogenesis. The effects of this increase in organic matter reactivity with permafrost thaw could intensify the increases in CH<sub>4</sub> and CO<sub>2</sub> release already predicted due to increasing temperatures, permafrost carbon mobilization, and waterlogging-induced changes in redox conditions.

Author contributions: S.B.H., P.M.C., S.R.S., V.I.R., and J.P.C. designed research; S.B.H., M.M.T., C.K.M., T.A.L., V.I.R., and J.P.C. performed research; M.M.T., T.A.L., and J.P.C. contributed new reagents/analytic tools; S.B.H. and M.M.T. analyzed data; and S.B.H., M.M.T., P.M.C., V.I.R., and J.P.C. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission. N.R. is a guest editor invited by the Editorial Board.

<sup>1</sup>To whom correspondence may be addressed. E-mail: sbh10c@fsu.edu or jchanton@fsu.edu.

This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1314641111/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1314641111/-DCSupplemental).

**Table 1.** Sites selected for study, in order of thaw stage; detailed descriptions of each site (with justification their positions in the thaw sequence) are given in Table S1

| Site name            | Habitat classification | Dominant vegetation                            | pH  |
|----------------------|------------------------|--|-----|
| PHS                  | Collapsed palsa        | <i>E. vaginatum</i> , woody species            | 4.1 |
| PHB                  | Collapsed palsa        | <i>E. vaginatum</i> , floating <i>Sphagnum</i> | 4.1 |
| Bog1                 | Bog                    | <i>Sphagnum</i> spp.                           | 4.2 |
| SOS                  | Bog                    | <i>Sphagnum</i> spp.                           | 4.0 |
| S (triplicate cores) | Bog                    | <i>Sphagnum</i> spp.                           | 4.2 |
| EOS                  | Fen                    | <i>E. angustifolium</i> , <i>Sphagnum</i> spp. | 4.8 |
| E (triplicate cores) | Fen                    | <i>E. angustifolium</i>                        | 5.8 |
| Fen1                 | Fen                    | <i>C. rostrata</i>                             | 6.0 |
| Fen2                 | Fen                    | <i>E. angustifolium</i>                        | 5.7 |

(FT-ICR MS) of DOM. Our study specifically addresses the effect of thawing permafrost, and its attendant shifts in hydrology and plant communities, on  $\text{CH}_4$  and  $\text{CO}_2$  production potentials and mechanisms, via changes in organic matter chemical composition (commonly referred to as organic matter “quality”) in a thawing peatland complex.

### Study Site and Habitat Classification

Stordalen Mire (68.35°N, 19.05°E) is a peat plateau in northern Sweden with a peat depth ranging from 1 to 3 m (22). The ground’s thaw state and consequent relationship to the water table determine the plant community, which in turn determines organic matter composition (21). Detailed vegetation surveys and analyses of aerial photographs taken at Stordalen (22–24) have demonstrated that permafrost thaw between 1970 and 2000 has caused dry permafrost hummocks to decrease in area by 10%, giving way to wetter minerotrophic sites, which increased by 17% (24). These changes have been accompanied by shifts in plant community from shrubs and lichens in permafrost hummocks to *Sphagnum* spp. in wetter sites followed by evolution to tall graminoid species as thaw-induced subsidence increases (22–24). Our site selections are based on these studies, which provide direct evidence that at minimum, six of our sites (Table 1 and Table S1) were once palsa (sites named PHS, PHB, S, and E) or likely palsa (sites named Bog1 and Fen1) underlain by permafrost (22–24). Similar processes are known to occur in other Arctic peatlands, where permafrost thaw creates wet depressions that are colonized first by *Sphagnum* and then by sedge species as the ground collapses with increasing thaw (25–27).

For this study, habitats were classified as “palsa,” “collapsed palsa,” “bog,” or “fen.” The palsa, bog, and fen classifications correspond, respectively, to the dry ombrotrophic (I), combined semiwet and wet ombrotrophic (II and III), and tall graminoid minerotrophic (IV) classifications of Johansson et al. (22) and represent a thaw gradient of increasing active layer depth. To these we added the additional designation of collapsed palsa for recently thawed waterlogged thermokarst sinkholes surrounded by palsa. Vegetation in these collapsed palsa sites is generally more diverse than that in the other three habitats, ranging from woody shrubs and *Eriophorum vaginatum* where the water table

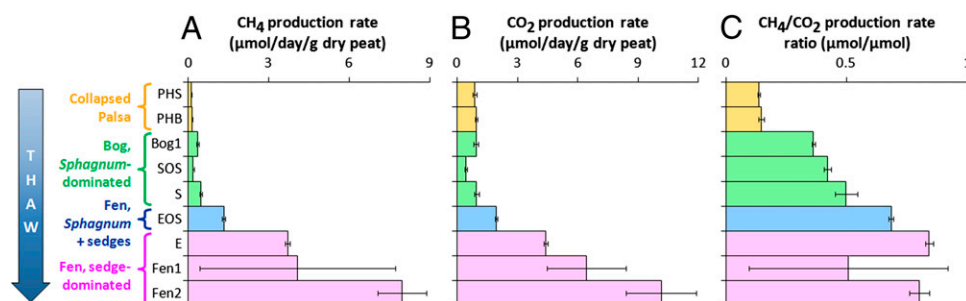
is at or just below the peat surface to floating *Sphagnum* mats where the water table is at or above the peat surface. Over time, vegetation in collapsed palsa may shift toward domination by nonfloating *Sphagnum* spp. (more bog-like) or sedges (more fen-like). Although permafrost thaw does not necessarily progress through all of these stages—for instance, rapid thaw may create a collapsed palsa sinkhole, which subsequently becomes more like a bog or a fen, whereas more gradual thawing may skip the collapsed palsa stage and cause more gradual changes in vegetation—these stages represent a thaw progression based on the possible shifts in vegetation and hydrology. Following a temporal succession of apparent time since onset of thaw, the habitats are ordered: (i) palsa, (ii) collapsed palsa, (iii) bog, and (iv) fen.

We selected nine sites spanning the thaw progression from collapsed palsa to fen (Table 1 and Table S1). Intact palsa sites were not included in this study because their dry, aerobic status prevents meaningful comparison with other sites based on anaerobic incubations and DOM measurements. Previous measurements of  $\text{CH}_4$  and  $\text{CO}_2$  fluxes from palsas have shown that they produce negligible amounts or even consume ambient  $\text{CH}_4$  (23, 28, 29) but are a net source of  $\text{CO}_2$  (28).

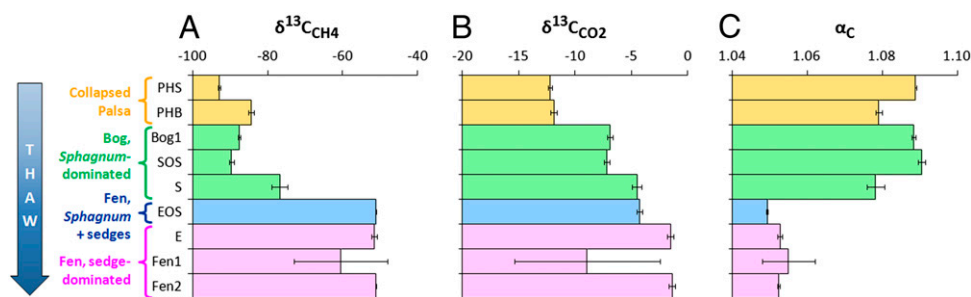
### Results

**Thaw Increases Potential  $\text{CH}_4$  and  $\text{CO}_2$  Production.** Anaerobic incubations (Fig. S1) reveal significant increases in potential  $\text{CH}_4$  and  $\text{CO}_2$  production and  $\text{CH}_4/\text{CO}_2$  ratios along the thaw progression ( $P < 0.0001$  for all of these trends) (Fig. 1 and Fig. S2).

**Thaw Shifts Methanogenesis to the Acetoclastic Pathway.**  $\delta^{13}\text{C}$  and  $\alpha_C$  of incubation  $\text{CH}_4$  and  $\text{CO}_2$  are shown in Fig. 2. Higher  $\alpha_C$  (and more negative  $\delta^{13}\text{C}_{\text{CH}_4}$ ) indicates a higher proportion of hydrogenotrophic methanogenesis, whereas lower  $\alpha_C$  (and less negative  $\delta^{13}\text{C}_{\text{CH}_4}$ ) implies more acetoclastic methanogenesis (10, 12). The incubations fall into two groups (Fig. 2C) with a significant ( $P < 0.0001$ ) separation in  $\alpha_C$  values: collapsed palsa and bog peat with  $\alpha_C$  between 1.075 and 1.092, and fen peat with  $\alpha_C$  between 1.048 and 1.062. This result suggests a distinct shift from hydrogenotrophic to acetoclastic methanogenesis along the thaw progression associated with increasing organic matter lability (Fig. 1A and B) and increasing pH (Table 1).  $\delta^{13}\text{C}_{\text{CO}_2}$  (Fig. 2B)



**Fig. 1.**  $\text{CH}_4$  and  $\text{CO}_2$  production rates in anaerobic incubations ( $\pm$ SE between replicates), which represent relative organic matter lability as potential decomposition rates. Samples are grouped into categories and placed in hypothesized order of permafrost thaw progression as described in Table 1 and Table S1. (A)  $\text{CH}_4$  production rates, (B)  $\text{CO}_2$  production rates, and (C) ratios of  $\text{CH}_4/\text{CO}_2$  production.



**Fig. 2.** Carbon isotopic composition of  $\text{CH}_4$  and  $\text{CO}_2$  produced in anaerobic incubations ( $\pm$ SE between replicates): (A)  $\delta^{13}\text{C}_{\text{CH}_4}$ , (B)  $\delta^{13}\text{C}_{\text{CO}_2}$ , and (C)  $\alpha_C$ , defined as  $(\delta^{13}\text{C}_{\text{CO}_2} + 1,000)/(\delta^{13}\text{C}_{\text{CH}_4} + 1,000)$ .  $\alpha_C$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  imply a shift in methanogenesis from hydrogenotrophy to acetoclasty along the thaw gradient associated with increasing pH and organic matter lability. Increasing  $\delta^{13}\text{C}_{\text{CO}_2}$  is consistent with increasing  $\text{CH}_4/\text{CO}_2$  production ratios (Fig. 1C) (17).

also increases along the thaw progression, consistent with the increasing  $\text{CH}_4/\text{CO}_2$  ratio (Fig. 1C) and reflecting an increasing proportion of methanogenesis-derived  $\text{CO}_2$  (17).

**Peat C/N Ratios Reflect Plant Community Shifts.** C/N ratios (by weight) of the peat used in the incubations are highest in bogs, intermediate in collapsed palsas, and lowest in fens (Fig. 3A). This trend is consistent with shifts in plant litter quality along the thaw sequence. Living plant samples of dominant Stordalen species collected at the Marcell Experimental Forest (northern Minnesota) showed a similar pattern in C/N ratios, from *E. vaginatum* (common in intact palsas, collapsed palsas, and bogs;  $\text{C/N} = 39 \pm 24$ ), through *Sphagnum* spp. (common in bogs;  $\text{C/N} = 46 \pm 18$ ), *Eriophorum angustifolium* (common in fens;  $\text{C/N} = 19 \pm 0.4$ ), and *Carex* spp. (common in fens;  $\text{C/N} = 25 \pm 3$ ).

**Peat Becomes More Labile Across the Thaw Gradient.** To investigate the structure of the peat organic matter, we used FTIR spectroscopy to examine: (i) surface peat (<10 cm, average ~3 cm); (ii) near-surface peat used in incubations, sampled just below the water table, examined preincubation (<22 cm, average ~11 cm); and (iii) deeper peat (24–35 cm, average ~25 cm) (Table S2). Whereas the spectra are generally similar between samples, the relative intensity of particular bands differs (Fig. 4), revealing the nature of chemical changes during peat development and humification (30). Along the thaw progression, carboxylic acid bands [ $1,720\text{ cm}^{-1}$  (31–34); Fig. 4A] weaken, likely because the fens' higher pH (Table 1) maintains organic acids as nonvisible carboxylate anions. Surface fen peat had more abundant polysaccharides [ $1,030\text{--}1,080\text{ cm}^{-1}$  (35)] and less abundant lignins [ $1,513\text{--}1,515\text{ cm}^{-1}$  (33)], aromatics [ $1,600\text{--}1,650\text{ cm}^{-1}$  (31)], and aliphatics [ $2,850$  and  $2,920\text{ cm}^{-1}$  (31)] than deep fen peat, indicating more cellulose (O-alkyl-C) plant material in the former vs. more decomposed, humified structures in the latter (Fig. 4B; less-pronounced differences were seen in bog and collapsed palsa peat).

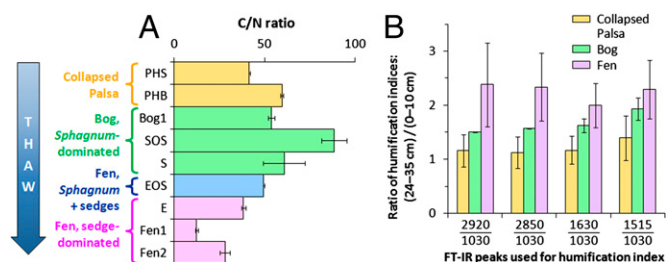
To further identify the FTIR spectral differences between peat in different habitats, we calculated ratios of aliphatic, aromatic,

and phenolic moieties to polysaccharides (Table S2), defined as humification indices (HI) (36) because they tend to increase with decomposition in soils. Across the sites, the surface and near-surface peat lacked consistent differences in HI; however, in the deep peat, fen HIs (except site E) were higher than collapsed palsa and bog HIs, suggesting more advanced decomposition in deep fen peat (Table S2). (In fen site E, remnant *Sphagnum* at depth resulted in an HI similar to deep bog samples, because HI reflects both source plant material and decomposition.) Consistent with increased decomposition with depth, most HIs were higher in deep than in surface peat (Table S2; see also Fig. 4B). This change can be quantified as a humification rate by calculating the ratio of deep to surface HI (24–35 cm vs. 0–10 cm), with higher ratios implying higher rates of humification through the soil column (i.e., faster decomposition over time). Humification rates with respect to all wavenumbers increased along the thaw progression, with the greatest increases occurring for the transformation of polysaccharides into aliphatic moieties ( $2,920$  and  $2,850\text{ cm}^{-1}$ ) (Fig. 3B).

**DOM Chemistry Changes with Thaw.** To investigate the structure of DOM, pore water samples spanning the thaw progression were analyzed by FT-ICR MS, of which representative bog (SOS site, 31 cm) and fen (E site, 25.5 cm) samples are shown (Fig. 5 and Fig. S3; Table 2). Peaks were assigned molecular formulas, taking into account C, H, O, N, and S (total 21,114 compounds; 11,527 bog and 9,587 fen), which were classified based on their N and S content and H/C and O/C ratios (Table 2). Sixty-four percent of compounds (13,436/21,114) were present in both samples (i.e., matching). To visualize differences in DOM composition, compounds that were unique to each sample (i.e., nonmatching) are plotted by their H/C vs. O/C ratios and molecular size (Fig. 5).

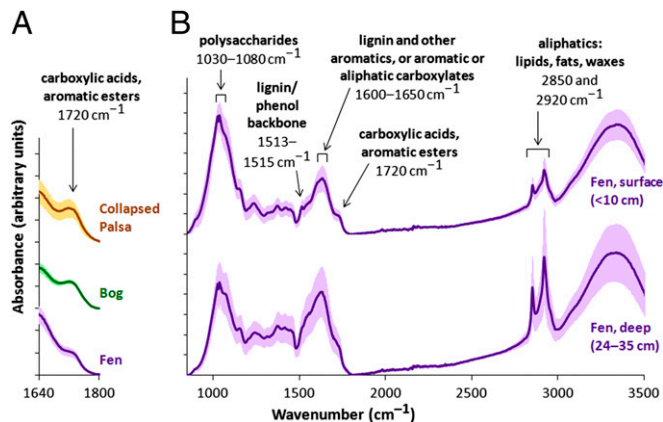
DOM compositional differences are clear between bog and fen sites. In the SOS/E site comparison (Fig. 5 and Fig. S3; Table 2), this is despite E's presence of remnant *Sphagnum* at depth, revealing that DOM at depth (unlike solid peat) is shaped by surface vegetation (39) even when buried remnants of older vegetation are present. Two distinct compound classes can be seen in both samples (Fig. 5A): class 1, occupying most of the plot area and representing various aliphatics, lignins, and tannins, and class 2 in the lower left-hand corner ( $\text{O/C} = 0\text{--}0.4$ ,  $\text{H/C} = 0\text{--}0.8$ ) representing condensed aromatic structures (37). Within both classes, O/C ratios are lower in fen than in bog DOM. Specifically, fen DOM contained more lipid-, other low-O/C-, protein- and amino sugar- (AS), and lignin-like compounds, whereas bog DOM contained more condensed aromatic and tannin-like compounds (Table 2 and Fig. 5A) (37). Fen DOM also had a lower average molecular size than bog DOM (Fig. 5B).

To characterize the oxidation states and unsaturation of the compounds comprising DOM, the double-bond equivalence (DBE), i.e., the total number of double bonds and aliphatic rings in each molecular formula, was calculated. The DBE distribution in bog DOM is skewed toward higher values compared with fen DOM (Fig. S3A), indicating that bog DOM is more unsaturated overall. To characterize  $\text{C}=\text{C}$  bonds and rings,  $\text{DBE}-\text{O}$  was calculated as the number of oxygen atoms subtracted from DBE



**Fig. 3.** Peat chemistry changes with thaw. (A) C/N weight ratios ( $\pm$ SE) of preincubation peat. (B) Ratios of deep (24–35 cm) to surface (<10 cm) peat HI for each site category ( $\pm$ SE), representing humification rates, for several wavenumbers (Fig. 4B) with respect to polysaccharides ( $1,030\text{ cm}^{-1}$ ). The bog category excludes site S (which had no samples below 21 cm), and the fen category excludes site E (which had *Sphagnum* remains at depth).





**Fig. 4.** Average peat FTIR absorption spectra, with between-site SEs as shaded areas. Spectra are stacked (i.e., absorbance = 0 at each apparent baseline) and sized to the same vertical scale. (A) Organic acids in incubated peat samples (preincubation) decrease with thaw from collapsed palsas ( $n = 2$ ) to bogs ( $n = 3$ ) to fens (including both sedge only and *Sphagnum* + sedge;  $n = 4$ ). (B) In fens (excluding site E, which had *Sphagnum* remains at depth), humification leads to spectral changes between surface ( $n = 3$ ) and deep ( $n = 3$ ) peat. References for wavenumbers: see Results. Peat Becomes More Labile Across the Thaw Gradient.

under the assumption that most DOM oxygen is bound to carbon by a double bond (40, 41). In contrast with DBE, the DBE–O distribution is lower in bog than in fen DOM (Fig. S3B). This difference between the DBE and DBE–O distributions indicates that bog DOM contains more hydrophilic, oxygen-rich compounds than fen DOM, and that a larger portion of the unsaturation in bog DOM is due to C=O bonds (mostly from carboxylic acid) than in fen DOM (41, 42). The higher oxygen content of bog DOM, as evidenced by both its DBE/DBE–O distributions and its higher O/C ratios relative to fen DOM, indicate that bog DOM has a higher oxidation state than fen DOM.

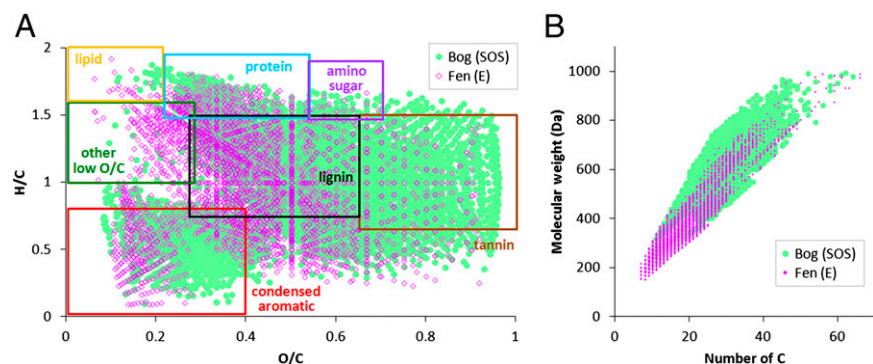
## Discussion

The increase in relative peat CH<sub>4</sub> and CO<sub>2</sub> production potentials (Fig. 1 A and B) along the thaw gradient when incubated under identical temperature and water saturation indicates an increase in organic matter lability. We propose three primary causes for this increase, all of which are tied to the changes in plant community associated with permafrost thaw: (i) increasing pH causes loss of organic acids that would otherwise inhibit microbial decomposition; (ii) decreasing peat C/N ratios increase organic matter quality by providing more abundant nitrogen; and (iii) increasing protein-like (and perhaps also relatively labile lipid-like) compounds in DOM may act as high-quality substrates for microbes. These changes can be directly observed in the chemical structure of peat and DOM along the thaw progression.

The types of compounds comprising organic matter help define its lability. For example, undissociated organic acids, particularly sphagnum acid and other *Sphagnum*-derived phenolics (43, 44), inhibit organic matter decay. The apparent increase in lability across the gradient could thus be due to a decrease in organic acids (Fig. 4A) driven by changing plant inputs and increasing pH (Table 1 and Table S1). However, pH's effect on decomposition (both directly through impacts on microbial activity and indirectly via shifting organic acids to their less inhibitory anionic forms) is unlikely to be the sole process governing decomposition rates in this system, given Ye et al.'s (45) demonstration that incubating bog peat at fen-typical pH did not stimulate fen-like CH<sub>4</sub> production to the levels seen in fen peat. Phenolic abundance may also decrease along the thaw sequence due to the enzymatic latch mechanism (46), whereby the enzyme phenol oxidase (which degrades phenolic compounds) depends on bimolecular oxygen availability. In fens, vascular plant roots may transport oxygen into the soil, where it activates phenol oxidase and thereby decreases the concentration of decomposition-inhibiting phenolics. Decreasing C/N ratios (Fig. 3A), driven by thaw-associated changes in plant community (from *E. vaginatum* and *Sphagnum* spp. to *E. angustifolium* and *Carex rostrata*) that lower the organic matter C/N ratio, may also increase organic matter lability by decreasing nitrogen limitation for decomposers.

Whereas the solid-phase peat represents an important substrate for decomposition, a large proportion of  $\text{CH}_4$  and  $\text{CO}_2$  production uses materials in the dissolved phase (39). This is particularly true in fens due to fen DOM's high lability (relative to bog DOM), such that the majority of fen respiration products is derived from DOM decomposition (39). We therefore analyzed DOM chemistry and reactivity in addition to peat chemistry and reactivity. The DOM chemical structure was markedly different between bog and fen (Fig. 5 and Fig. S3; Table 2), shaped in part by different plant source material. Decay-resistant tannins from *Sphagnum* were abundant in the bog, whereas the fen had a higher proportion of comparatively labile protein- and fatty-acid-like compounds possibly originating as sedge root exudates.

In addition to organic matter compositional differences that directly affect its lability, there are also differences indicating the degree of decomposition. Ratios of HI in deep vs. surface peat, which represent decomposition rates through the soil column, indicate that decomposition rates increase along the thaw progression (Fig. 3B). Analogous to the fens' higher solid-phase humification rates with respect to the accumulation of both lignin- and lipid-like moieties (Fig. 3B), fen DOM also has a higher percentage of dissolved lignin- and lipid-like compounds (some of which are recalcitrant and can accumulate) than bog DOM (Table 2), consistent with more advanced decomposition. Fen DOM also has a smaller average molecular size than bog DOM (Fig. 5B). This result is consistent with the size reactivity model, in which high molecular weight DOM is hydrolyzed into low molecular weight DOM, causing small refractory compounds to accumulate (38). Furthermore, because microbial biomass includes abundant lipid- and protein-like substances, these



**Fig. 5.** Analysis of molecular formulas found in DOM in representative bog (site SOS, 31 cm, green circles) and fen (site E, 25.5 cm, purple diamonds) samples. (A) Van Krevelen diagram of nonmatching formulas (those not shared between samples) in bog vs. fen DOM, labeled with the specific compound classes expected to occur in each region (37). Each point represents one molecular formula present in one sample, plotted by its O/C and H/C ratio. (B) Molecular size distribution of nonmatching formulas. Smaller molecules in fen DOM indicate more advanced decay compared with bog DOM (38).





Scientific Research Station for providing infrastructure for sampling. This research was funded by the US Department of Energy Office of Biological and

Environmental Research under the Genomic Science (Award DE-SC0004632) and Terrestrial Ecosystems Science (Contract ER65245) programs.

- Schuur EAG, et al. (2008) Vulnerability of permafrost carbon to climate change: implications for the global carbon cycle. *Bioscience* 58(8):701–714.
- McGuire AD, et al. (2009) Sensitivity of the carbon cycle in the Arctic to climate change. *Ecol Monogr* 79(4):523–555.
- Houghton RA (2007) Balancing the global carbon budget. *Annu Rev Earth Planet Sci* 35:313–347.
- Gorham E (1991) Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. *Ecol Appl* 1(2):182–195.
- Whiting GJ, Chanton JP (2001) Greenhouse carbon balance of wetlands: Methane emission versus carbon sequestration. *Tellus B Chem Phys Meteorol* 53(5):521–528.
- Matthews E, Fung I (1987) Methane emission from natural wetlands: Global distribution, area, and environmental characteristics of sources. *Global Biogeochem Cycles* 1(1):61–86.
- Crill PM, et al. (1988) Methane flux from Minnesota peatlands. *Global Biogeochem Cycles* 2(4):371–384.
- Shindell DT, et al. (2009) Improved attribution of climate forcing to emissions. *Science* 326(5953):716–718.
- Boden TA, Marland G, Andres RJ (2012) Global, regional, and national fossil-fuel CO<sub>2</sub> emissions. Carbon Dioxide Information Analysis Center (CDIAC). Available at [http://dx.doi.org/10.3334/CDIAC/00001\\_V2012](http://dx.doi.org/10.3334/CDIAC/00001_V2012). Accessed December 5, 2012.
- Whiticar MJ, Faber E, Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO<sub>2</sub> reduction vs. acetate fermentation—Isotope evidence. *Geochim Cosmochim Acta* 50(5):693–709.
- Whiticar MJ (1999) Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chem Geol* 161(1–3):291–314.
- Chanton JP, Chasar LC, Glaser P, Siegel D (2005) *Stable Isotopes and Biosphere-Atmosphere Interactions, Physiological Ecology Series*, eds Flanagan LB, Ehleringer JR, Pataki DE (Elsevier Academic, San Diego), pp 85–105.
- Sugimoto A, Wada E (1993) Carbon isotopic composition of bacterial methane in a soil incubation experiment: Contributions of acetate and CO<sub>2</sub>/H<sub>2</sub>. *Geochim Cosmochim Acta* 57(16):4015–4027.
- Hornbrook ERC, Longstaffe FJ, Fyfe WS (1997) Spatial distribution of microbial methane production pathways in temperate zone wetland soils: Stable carbon and hydrogen isotope evidence. *Geochim Cosmochim Acta* 61(4):745–753.
- Hornbrook ERC, Longstaffe FJ, Fyfe WS (2000) Evolution of stable carbon isotope compositions for methane and carbon dioxide in freshwater wetlands and other anaerobic environments. *Geochim Cosmochim Acta* 64(6):1013–1027.
- Shoemaker JK, Schrag DP (2010) Subsurface characterization of methane production and oxidation from a New Hampshire wetland. *Geobiology* 8(3):234–243.
- Corbett JE, et al. (2013) Partitioning pathways of CO<sub>2</sub> production in peatlands with stable carbon isotopes. *Biogeochemistry* 114(1–3):327–340.
- Hines ME, Duddleston KN, Rooney-Varga JN, Fields D, Chanton JP (2008) Uncoupling of acetate degradation from methane formation in Alaskan wetlands: Connections to vegetation distribution. *Glob Biogeochem Cycles* 22(2):GB2017.
- Hines ME, Duddleston KN (2001) Carbon flow to acetate and C<sub>1</sub> compounds in northern wetlands. *Geophys Res Lett* 28(22):4251–4254.
- Kotsyurbenko OR, et al. (2007) Shift from acetoclastic to H<sub>2</sub>-dependent methanogenesis in a West Siberian peat bog at low pH values and isolation of an acidophilic *Methanobacterium* strain. *Appl Environ Microbiol* 73(7):2344–2348.
- Turetsky MR (2004) Decomposition and organic matter quality in continental peatlands: The ghost of permafrost past. *Ecosystems (NY)* 7(7):740–750.
- Johansson T, et al. (2006) Decadal vegetation changes in a northern peatland, greenhouse gas fluxes and net radiative forcing. *Glob Change Biol* 12(12):2352–2369.
- Christensen TR, et al. (2004) Thawing sub-arctic permafrost: Effects on vegetation and methane emissions. *Geophys Res Lett* 31(4):L04501.
- Malmer N, Johansson T, Olsrud M, Christensen TR (2005) Vegetation, climatic changes and net carbon sequestration in a North-Scandinavian subarctic mire over 30 years. *Glob Change Biol* 11(11):1895–1909.
- Zoltai SC (1993) Cyclic development of permafrost in the peatlands of Northwestern Alberta, Canada. *Arct Alp Res* 25(3):240–246.
- Vitt DH, Halsey LA, Zoltai SC (1994) The bog landforms of continental western Canada in relation to climate and permafrost patterns. *Arct Alp Res* 26(1):1–13.
- Jorgenson MT, Racine CH, Walters JC, Osterkamp TE (2001) Permafrost degradation and ecological changes associated with a warming climate in central Alaska. *Clim Change* 48(4):551–579.
- Bäckstrand K, et al. (2010) Annual carbon gas budget for a subarctic peatland, Northern Sweden. *Biogeosciences* 7(1):95–108.
- Lupascu M, Wadham JL, Hornbrook ERC, Pancost RD (2012) Temperature sensitivity of methane production in the permafrost active layer at Stordalen, Sweden: A comparison with non-permafrost northern wetlands. *Arct Antarct Alp Res* 44(4):469–482.
- Silamiķele I, et al. (2010) In *Mires and Peat*, ed Kļaviņš M (University of Latvia Press, Riga, Latvia), pp 71–95. Available at [www.lu.lv/fileadmin/user\\_upload/lu\\_portal/projekti/vpp/kuudra/Miresandpeat/mires-peat\\_71-95.pdf](http://www.lu.lv/fileadmin/user_upload/lu_portal/projekti/vpp/kuudra/Miresandpeat/mires-peat_71-95.pdf). Accessed July 31, 2013.
- Niemeyer J, Chen Y, Bollag J-M (1992) Characterization of humic acids, composts, and peat by diffuse reflectance Fourier-transform infrared spectroscopy. *Soil Sci Soc Am J* 56(1):135–140.
- Haberhauer G, Rafferty B, Strebl F, Gerzabek MH (1998) Comparison of the composition of forest soil litter derived from three different sites at various decomposition stages using FTIR spectroscopy. *Geoderma* 83(3–4):331–342.
- Cocozza C, D'Orazio V, Miano TM, Shetyk W (2003) Characterization of solid and aqueous phases of a peat bog profile using molecular fluorescence spectroscopy, ESR and FT-IR, and comparison with physical properties. *Org Geochem* 34(1):49–60.
- Gondar D, Lopez R, Fiol S, Antelo JM, Arce F (2005) Characterization and acid-base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. *Geoderma* 126(3–4):367–374.
- Grube M, Lin JG, Lee PH, Kokorevicha S (2006) Evaluation of sewage sludge-based compost by FT-IR spectroscopy. *Geoderma* 130(3–4):324–333.
- Broder T, Blodau C, Biester H, Knorr KH (2012) Peat decomposition records in three pristine ombrotrophic bogs in southern Patagonia. *Biogeosciences* 9(4):1479–1491.
- Sleighter RL, Hatcher PG (2007) The application of electrospray ionization coupled to ultrahigh resolution mass spectrometry for the molecular characterization of natural organic matter. *J Mass Spectrom* 42(5):559–574.
- Burdige DJ, Gardner KG (1998) Molecular weight distribution of dissolved organic carbon in marine sediment pore waters. *Mar Chem* 62(1–2):45–64.
- Chanton JP, et al. (2008) Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands. *Glob Biogeochem Cycles* 22(4):GB4022.
- Gonsior M, et al. (2009) Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry. *Environ Sci Technol* 43(3):698–703.
- Tfaily MM, Podgorski DC, Corbett JE, Chanton JP, Cooper WT (2011) Influence of acidification on the optical properties and molecular composition of dissolved organic matter. *Anal Chim Acta* 706(2):261–267.
- Tfaily MM, Hodgkins S, Podgorski DC, Chanton JP, Cooper WT (2012) Comparison of dialysis and solid-phase extraction for isolation and concentration of dissolved organic matter prior to Fourier transform ion cyclotron resonance mass spectrometry. *Anal Bioanal Chem* 404(2):447–457.
- Mellegård H, Stalheim T, Hormazabal V, Granum PE, Hardy SP (2009) Antibacterial activity of sphagnum acid and other phenolic compounds found in *Sphagnum papillosum* against food-borne bacteria. *Lett Appl Microbiol* 49(1):85–90.
- Zaitseva N (2009) A polysaccharide extracted from *Sphagnum* moss as antifungal agent in archaeological conservation. Master's thesis (Queen's University, Kingston, Ontario, Canada). Available at <http://hdl.handle.net/1974/5392>. Accessed April 30, 2013.
- Ye R, et al. (2012) pH controls over anaerobic carbon mineralization, the efficiency of methane production, and methanogenic pathways in peatlands across an ombrotrophic–minerotrophic gradient. *Soil Biol Biochem* 54:36–47.
- Freeman C, Ostle N, Kang H (2001) An enzymic 'latch' on a global carbon store. *Nature* 409(6817):149.
- Brake M, Höper H, Joergensen RG (1999) Land use-induced changes in activity and biomass of microorganisms in raised bog peats at different depths. *Soil Biol Biochem* 31(11):1489–1497.
- Blazewicz SJ, Petersen DG, Waldrop MP, Firestone MK (2012) Anaerobic oxidation of methane in tropical and boreal soils: Ecological significance in terrestrial methane cycling. *J Geophys Res Biogeosci* 117(G2):G02033.
- Gupta V, et al. (2013) Stable isotopes reveal widespread anaerobic methane oxidation across latitude and peatland type. *Environ Sci Technol* 47(15):8273–8279.
- Whiticar MJ, Faber E (1986) Methane oxidation in sediment and water column environments—Isotope evidence. *Org Geochem* 10(4–6):759–768.
- Lovley DR, Coates JD, Blunt-Harris EL, Phillips EJP, Woodward JC (1996) Humic substances as electron acceptors for microbial respiration. *Nature* 382(6590):445–448.
- Heitmann T, Goldammer T, Beer J, Blodau C (2007) Electron transfer of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog. *Glob Change Biol* 13(8):1771–1785.
- Keller JK, Bridgman SD (2007) Pathways of anaerobic carbon cycling across an ombrotrophic–minerotrophic peatland gradient. *Limnol Oceanogr* 52(1):96–107.
- Blodau C, Deppe M (2012) Humic acid addition lowers methane release in peats of the Mer Bleue bog, Canada. *Soil Biol Biochem* 52:96–98.
- Symons GE, Buswell AM (1933) The methane fermentation of carbohydrates. *J Am Chem Soc* 55(5):2028–2036.
- Nilsson M, Öquist M (2009) *Carbon Cycling in Northern Peatlands, Geophysical Monograph Series*, eds Baird AJ, Belyea LR, Comas X, Reeve AS, Slater LD (American Geophysical Union, Washington, DC), pp 131–144.
- van Hulzen JB, Segers R, van Bodegom PM, Lefelaar PA (1999) Temperature effects on soil methane production: An explanation for observed variability. *Soil Biol Biochem* 31(14):1919–1929.
- Horn MA, Matthies C, Küsel K, Schramm A, Drake HL (2003) Hydrogenotrophic methanogenesis by moderately acid-tolerant methanogens of a methane-emitting acidic peat. *Appl Environ Microbiol* 69(1):74–83.
- Chanton JP (2005) The effect of gas transport on the isotope signature of methane in wetlands. *Org Geochem* 36(5):753–768.
- Glenn S, Heyes A, Moore T (1993) Carbon dioxide and methane fluxes from drained peat soils, southern Quebec. *Global Biogeochem Cycles* 7(2):247–257.
- Blodau C, Moore TR (2003) Experimental response of peatland carbon dynamics to a water table fluctuation. *Aquat Sci* 65(1):47–62.
- Blodau C, Basiliko N, Moore TR (2004) Carbon turnover in peatland mesocosms exposed to different water table levels. *Biogeochemistry* 67(3):331–351.
- Lee H, Schuur EAG, Inglett KS, Lavoie M, Chanton JP (2012) The rate of permafrost carbon release under aerobic and anaerobic conditions and its potential effects on climate. *Glob Change Biol* 18(2):515–527.