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Characterization of labile organic matter in Pleistocene permafrost (NE Siberia), using Thermally assisted Hydrolysis and Methylation (THM-GC-MS)

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ABSTRACT

Pleistocene yedoma sediments store large amounts of soil organic matter (SOM) and are vulnerable to permafrost degradation. Here we contribute to our understanding of yedoma SOM dynamics and potential response to thaw, by molecular characterization of samples from a 5.7 m yedoma exposure, as well as upper permafrost samples that were previously incubated, using Thermally assisted Hydrolysis and Methylation (THM-GC-MS). In general, the SOM is derived from aliphatic material (including cutin and suberin), phenols (lignin, sphagnum acid), polysaccharides and N-containing components (largely microbial SOM). Soil organic carbon (SOC) content and molecular SOM composition follow a sawtooth pattern where local maxima in SOC coincide with lignin and aliphatic material that experienced only slight degradation, and minima with degraded plant-derived SOM and microbial tissue, representing a stratified cryopedolith. The SOC-depleted top 0.9 m (active layer and transition zone) is enriched in microbial SOM probably due to recent thawing. Comparison with CO_2 respiration rates indicates that SOM of microbial origin (low C/N) is more labile than aliphatic SOM from well-preserved plant tissue (high C/N). However, we argue that the more stable aliphatic SOM in SOC-rich layers might also be vulnerable to decay, which could, due to its abundance in SOC-rich layers, dominate overall Yedoma C losses due to thermal erosion.

1. Introduction

Yedoma deposits consist of fine-grained, ice-rich sediments that formed by predominantly wind-driven accumulation and consequent syngenetic permafrost aggradation during the late Pleistocene (Grosse et al., 2013; Schirrmeister et al., 2013; Murton et al., 2015). Organic matter burial caused by steady eolian deposition over long periods of time, in combination with cryoturbation, have resulted in the sequestration of large amounts of soil organic carbon (SOC). These C-rich, loess-like deposits are widespread in unglaciated regions in northeastern Russia, and Alaska (Beringia), where they are referred to as Yedoma or Ice Complex (Schirrmeister et al., 2013). The high ice content in Yedoma is a result of its fine texture and mostly syngenetic permafrost aggradation, creating suitable conditions for ground ice development (Gilbert et al., 2016). The area where Yedoma occurs, or *Yedoma core region* (Siberia and Alaska combined), covers c. 1.4 million km^2 (Hugelius et al., 2014), of which c. 30% (416,000 km^2) is considered *intact*, or *undisturbed* Yedoma (Fig. 1a). The remaining area has undergone thermo-erosion, and consists mainly of refrozen thermokarst deposits (56%) also known as alas complex deposits or alasses, and thermokarst lakes (10%; Strauss et al., 2013; Hugelius et al., 2014; Walter Anthony et al., 2014). The core region is known to contain substantial amounts of soil organic matter (SOM), currently estimated at c. 211 Gt SOC (Strauss et al., 2013; Hugelius et al., 2014), of which c. 83 Gt is stored in undisturbed Yedoma (Strauss et al., 2013). A recent study by Shmelev et al. (2017) identifies expected overestimations in earlier studies, and finds considerably lower SOC content in Yedoma in northeastern Siberia, reporting intact Yedoma in NE Siberia to contain 3.9 Gt C, with an additional 15.7 Gt C in refrozen thermokarst basins. Considering its relative spatial scarcity, intact Yedoma stores relatively more SOC than the geographically predominant alas basin sediments, which is in line with studies showing that refrozen thermokarst deposits contain c. 28% less SOC than adjacent intact sites (Zimov et al., 2006b; Walter Anthony et al., 2014). Contrarily, others like Strauss et al.

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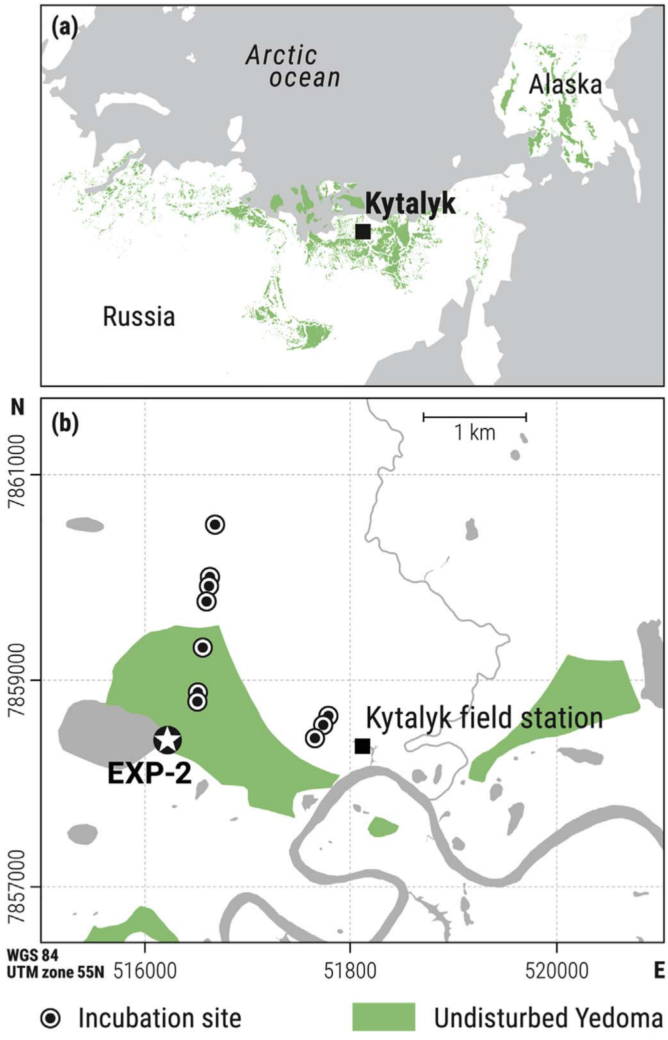

Fig. 1. (a) Distribution of undisturbed yedoma sediments in the *Yedoma core region* (data from Strauss et al., 2016). (b) Location of exposure EXP-2 and incubation sites.

(2013) found c. 50% higher SOC content in refrozen thermokarst sediments compared to intact Yedoma, caused by Holocene soil and peat formation, and reworking. Shmelev et al. (2017) found only slightly higher C content in alas complex deposits, but emphasize the higher regional heterogeneity within alas sites, caused by the high variability in local biologic productivity and peat formation, compared to sites with intact Yedoma deposits. Although pedogenesis takes place during syngenetic cryo-sequestration of Yedoma, it often does not appear in distinct soil horizons, and yedoma SOM is generally considered to be C-rich (high C/N) and little-decomposed (Zimov et al., 2006a; Gubin and Veremeeva, 2010; Hugelius et al., 2012). Phases of reduced sedimentation rates and incipient pedogenesis during periods of predominantly syngenetic permafrost aggradation are referred to as cryopedolith formation (Gubin, 1994; 2002 in Murton et al., 2015). Evidence of more profound pedogenetic processes (e.g., buried paleosols, fossil rodent burrows, and thaw unconformities) indicate strong paleoenvironmental variation during the Late Pleistocene, including cyclic stages of thermokarst activity (Zanina et al., 2011; Schirrmeister et al., 2013; Murton et al., 2015; Weiss et al., 2016).

SOC content in yedoma deposits is relatively high, between 1 and 5% (Zimov et al., 2006a; Schirrmeister et al., 2013; Shmelev et al., 2017), with peaks for certain stratigraphic units (Schirrmeister et al., 2011a; Murton et al., 2015). Yedoma SOM is generally considered to be susceptible to decomposition (Zimov et al., 2006a; Strauss et al., 2015), a view that is supported by empirical evidence of extensive greenhouse gas release from thawing permafrost under thermokarst lakes (Walter et al., 2006, 2007). Increased greenhouse gas release from thawing permafrost could thereby accelerate climate change through a permafrost carbon feedback (Zimov et al., 2006a; Kuhry et al., 2010; Schuur et al., 2015).

Permafrost SOM studies frequently apply a combination of elemental analysis of C, nitrogen (N), C/N, and the stable isotope ratios δ^{13}C and δ^{15}N (Kuhry and Vitt, 1996; Schirrmeister et al., 2011a, b; Hugelius, 2012; Strauss et al., 2015). Less common are spectroscopic methods (Waldrop et al., 2010; Höfle et al., 2013), molecular composition data of targeted lipid extracts (Routh et al., 2014; Strauss et al., 2015), and characterizations of macromolecular SOM, except for lignin analyses using CuO oxidation in permafrost peat (e.g. Routh et al., 2014).

In this study we determine macromolecular SOM composition using Thermally assisted Hydrolysis and Methylation (THM) hyphenated with gas chromatography and mass spectrometry (THM-GC-MS), with tetramethyl ammonium hydroxide (TMAH) as derivatizing reagent. With THM, the strongly alkaline aqueous TMAH initiates hydrolytic cleavage followed by dissociation of ammonium salts through flash heating (at 300–700 °C) and methylation of functional groups such as hydroxyl to methoxyl, and carboxyl to methyl ester (Challinor, 2001; Klingberg et al., 2005). This method has been used frequently for SOM fingerprinting (Shadkami and Helleur, 2010; Schulten and Sorge, 1995), and has the advantage over conventional analytical pyrolysis (without TMAH) that it has enhanced sensitivity of functional groups in polyphenolic constituents, such as lignin and tannin (Martin et al., 1977; Del Río and Hatcher, 1998; Chefetz et al., 2000; Filley et al., 2000), and aliphatic constituents such as cutin and suberin (Nierop, 1998). THM-GC-MS is furthermore effective in detecting other biocomponents, such as polysaccharides (Fabbri et al., 1996; Tanczos et al., 2003; Schwarzinger, 2004), and amino acids (Hendricker and Voorhees, 1998; Knicker et al., 2001). As far as we know, THM-GC-MS has thus far not been used to characterize yedoma SOM.

In a previous study, Weiss et al. (2016) discussed gravimetric (bulk density), elemental (C and N) and stable isotopic (δ^{13}C and δ^{15}N) composition of a 5.7 m deep profile in mostly undisturbed Yedoma in Kytalyk (NE Siberia, Russia). Supported by data from nearby upper permafrost field incubations, they showed that SOM-depleted samples (low SOC content) were comparatively enriched in N (low C/N) and in biolabile SOM components, resulting in high initial (c. 72 h incubation) CO_2 production after thawing. The same SOC-depleted samples with labile SOM, had been more strongly affected by microbial activity (recognized from higher δ^{13}C) than the SOC-rich samples that contained less decomposed and more recalcitrant materials. This effect might be less pronounced over longer incubation periods, when a lack of available SOM is expected to limit long-term CO_2 production, and—over time—C/N ratios are positively correlated with C loss (Schädel et al., 2014). Nonetheless, significantly higher initial CO_2 production rates indicate the presence of labile SOM components in SOC-poor upper permafrost material. To test this hypothesis and to improve our general understanding of SOM characteristics and dynamics in yedoma soils and sediments, we used THM-GC-MS to characterize the exposure in yedoma deposits from Weiss et al. (2016) and the upper permafrost samples that were used for incubation experiments in that study.

2. Materials and methods

2.1. Study site and sample selection

The study area is located in the Kytalyk Wildlife Reserve (70.83 °N, 147.49 °E; 11 m a.s.l.) in the Yedoma core region (NE Siberia, Russia; Fig. 1a), and is underlain by continuous permafrost. The tundra vegetation on the Yedoma uplands in Kytalyk consists primarily of dwarf shrub, lichen, and sedge (Siewert et al., 2015). *Sphagnum* is common in the wet thermokarst basins, but currently not present on the well-