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Organic matter characteristics in yedoma and thermokarst deposits on Baldwin Peninsula, west Alaska

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1 Supporting methodology descriptions

1.1 Grain size analysis

The analysis of grain size is important in identifying the origin of sedimentary deposits: grain size distributions of the sedimentary sediments can give insights into the medium of transportation, as well as the depositional mechanism. Grain size was analyzed for yedoma exposure BAL16-B2 and drained thermokarst lake basin exposure BAL16-B4. In order to only measure the clastic material, organic matter was removed from the samples by treating the samples with hydrogen peroxide (H_2O_2). For this, about 10 ml of sample material was weighed into 400 ml beakers to which 100 ml of 3% H_2O_2 and 4 drops of ammonia were added. The beakers were then placed on a shaker at 60°C for 2-3 weeks. Five times a week, the beakers were cleaned and 10 ml of H_2O_2 was added (once the reaction was less strong 20 ml was added). The pH was kept between 6 and 8 by adding ammonia or acetic acid to allow an optimal reaction. After the complete removal of the organic material, the samples were washed with about one liter of purified water to remove the H_2O_2. The samples were then centrifuged (Cryofuge 8500i for 10 minutes at 5050 RPM, 20°C; Multifuge 3-S Heraeus 2-3 times for 15 minutes at 4000 RPM) and freeze-dried. The samples were manually homogenized and about 1 gram was weighed into 250 ml plastic bottles and a spoon spatula of dispersing agent (tetrasodium pyrophosphate, $Na_4P_2O_7$) was added. The bottles were filled with an ammonia solution (10 ml NH_4OH in 100 liter of water) and placed in an overhead shaker overnight. As a last step before measuring, the samples were split into 8 homogeneous samples to enable measurement of samples with sediment concentrations between 5-15%. The material was hereby also sieved for >1 mm to avoid damage to the laser. Inorganic particles >1mm were weighed and if the residue was significant compared to the sample, it was included in the distribution afterwards. The grain size was analyzed with the Malvern Mastersizer 3000 laser. The device cleans automatically and measures background scatter. After a sample is inserted into the dispersion unit, it is channeled through the device to the measurement cell where it is exposed to a red laser and blue led (633 nm and 470 nm), of which the scatter is measured by the detectors. The average is calculated of three measurements per split sample (standard deviation <10%). Grain size statistics are calculated using the software GRADISTAT using the grain size scaling from Blott & Pey (2001).

1.2 Elemental analysis

Total carbon (TC), total nitrogen (TN) and total organic carbon (TOC) are measured based on the principle of combustion chromatography. TC and TN were determined using the Elementar Vario EL III. A subsample of each homogenized sample was weighed into small tin capsules in duplicate. A blank capsule was measured in the beginning for background detection and a calibration run was performed before and after every fifteen samples. The percentage of total carbon and nitrogen was calculated. The determination of TOC was done using the Elementar Vario Max C. Depending on the TC values, fifteen to hundred milligrams of the samples was weighed into crucibles and placed into the machine. TN, TC and TOC are expressed in weight percentage (wt%).

Stable carbon isotopes ($\delta^{13}C$) could be measured after the removal of carbonates. This was done by treating the samples with 20 ml hydrogen chloride for three hours at 97.7°C. Purified water was added and the samples were decanted and washed three times. When the chloride content was under 500 parts per million, the samples were filtered over a glass microfiber filter (Whatman Grade GF/B, nominal particle retention of 1.0 µm). Afterwards, the residue was dried in a drying cabinet at 50°C. Dry samples were ground manually and weighed into tin capsules. The required sample weight was calculated by dividing 20 by the TOC value. A ThermoFisher Scientific Delta-V-Advantage gas mass spectrometer equipped with a FLASH elemental analyzer EA 2000 and a CONFLO IV gas mixing system was used to determine the $\delta^{13}C$. In this system, the sample is combusted at 1020°C so that the OC is transferred to CO_2, after which the isotope ratio is determined relative to a laboratory standard of known isotopic composition. Capsules for control and calibration were run in between. The unit is per mille (‰) and the ratio is compared to the standard established from the Pee Dee Belemnite (VPDB: a limestone formation of which the ratio was set to 0).

1.3 Lipid biomarker analysis

From the GDGT concentration, the branched and isoprenoid tetraethers (BIT) index was calculated following Eq. (1).

$$BIT = \frac{Ia+IIa+IIIa}{Ia+IIa+IIIa+crenarchaeol} \tag{1}$$

The BIT index is the ratio between the mainly terrestrially produced brGDGTs and crenarchaeol (Figure S1), an isoprenoid GDGT which is most abundant in marine and lacustrine environments. Apart from the use of this proxy to distinguish between terrestrial and marine sources (Hopmans et al., 2004), the ratio is correlated to precipitation (Dirghangi et al., 2013). The methylation of branched tetraethers (MBT) index is the ratio between brGDGT-I and -II structures and was calculated according to Peterse et al. (2012) following Eq. (2).

$$MBT = \frac{Ia+Ib+Ic}{Ia+Ib+Ic+IIa+IIb+IIc+IIIa} \tag{2}$$

This ratio can be used in paleoreconstructions. Weijers et al. (2007) found that Arctic soils are generally dominated by brGDGTs with additional methyl branches and suggested that more methyl branches are formed in lower temperatures.

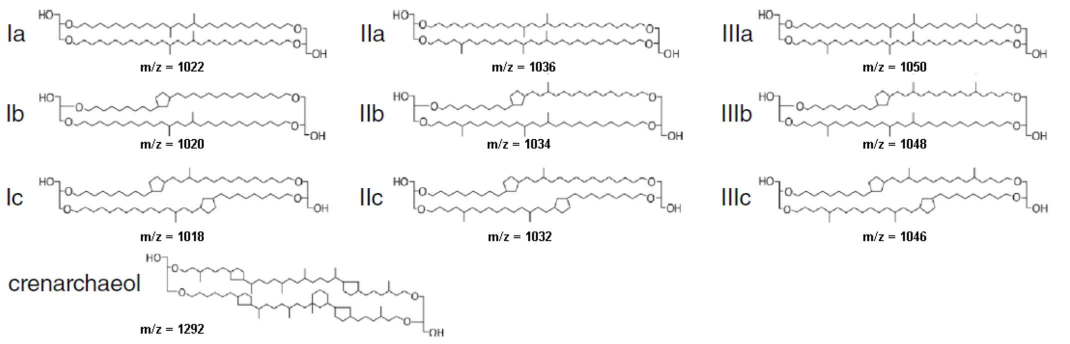

Figure S1: Molecular structures of brGDGTs and crenarchaeol with mass-to-charge ratio (m/z). The structures differ in mass by the presence of cyclopentane moieties (a, b, c) and the number of methyl branches (I, II, III). From Peterse et al. (2014).

2 Supporting figures and tables

2.1 Photographs field sites

Photographs of the field sites are shown for the yedoma exposure BAL16-B2 (Figure S2), drained thermokarst lake basin exposures BAL16-B3 (Figure S3) and BAL16-B4 (Figure S4) and the thermokarst lake core BAL16-UPL-L1 (Figure S5).

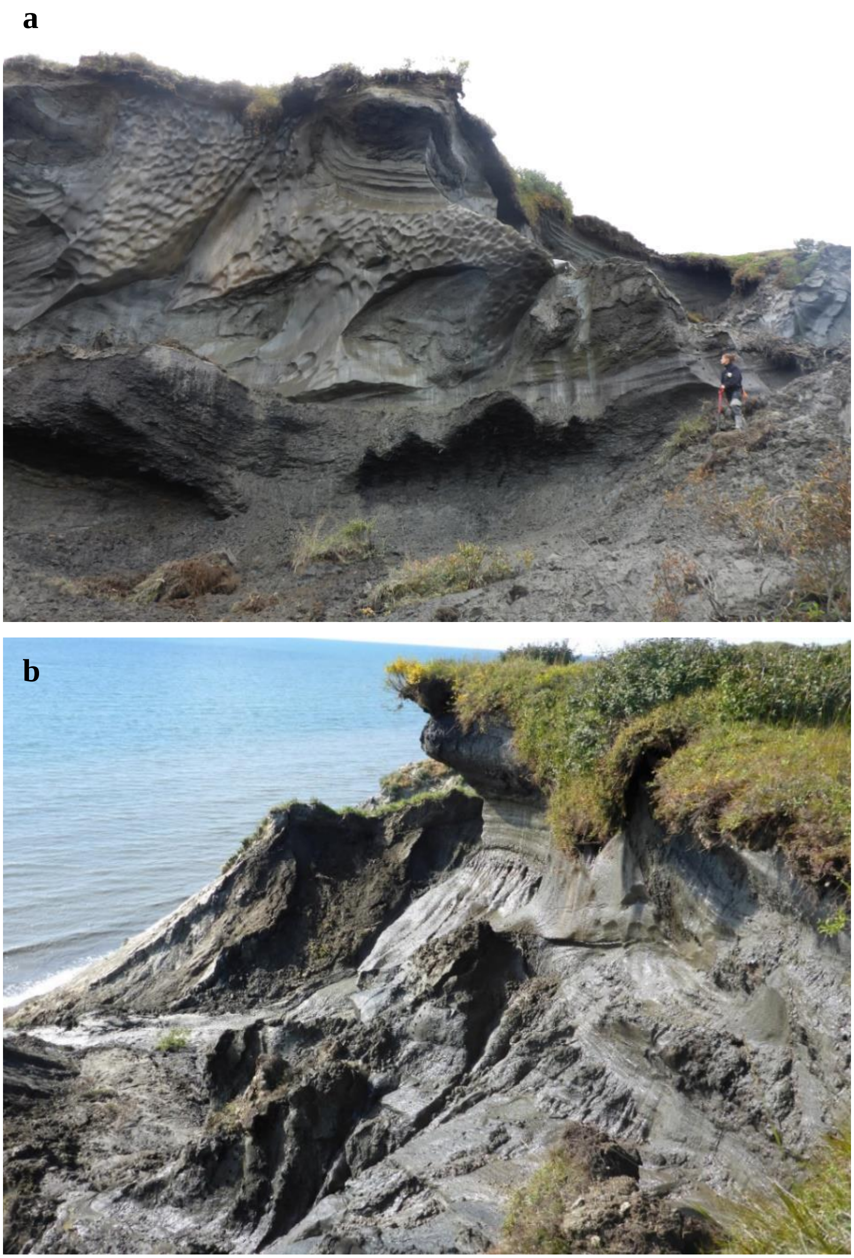

Figure S2: Yedoma exposure BAL16-B2 from the front (a) and side (b). Photos by J. Strauss, August 2016.

Figure S3: Drained thermokarst lake basin exposure BAL16-B3. Photo by J. Strauss, August 2016.

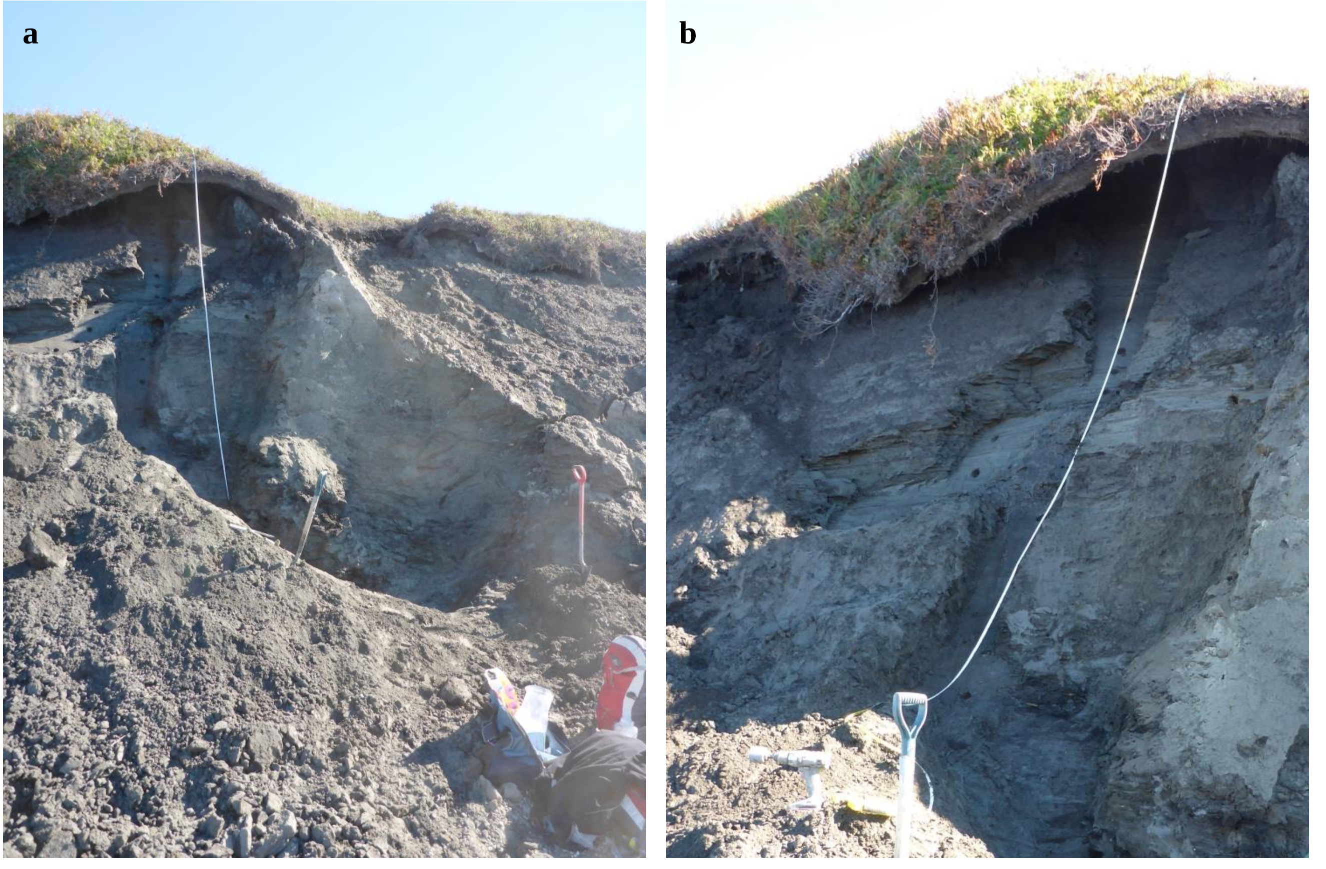

Figure S4: Drained thermokarst lake basin exposure BAL16-B4 from the front (a) and side (b). Photos by J. Strauss, August 2016.

Figure S5: Thermokarst lake core BAL16-UPL1-L1. Photo by J. Lenz, December 2016.

2.2 Total organic carbon

Figure S6 shows variations in total organic carbon of previously studied yedoma deposits in Siberia and Alaska.

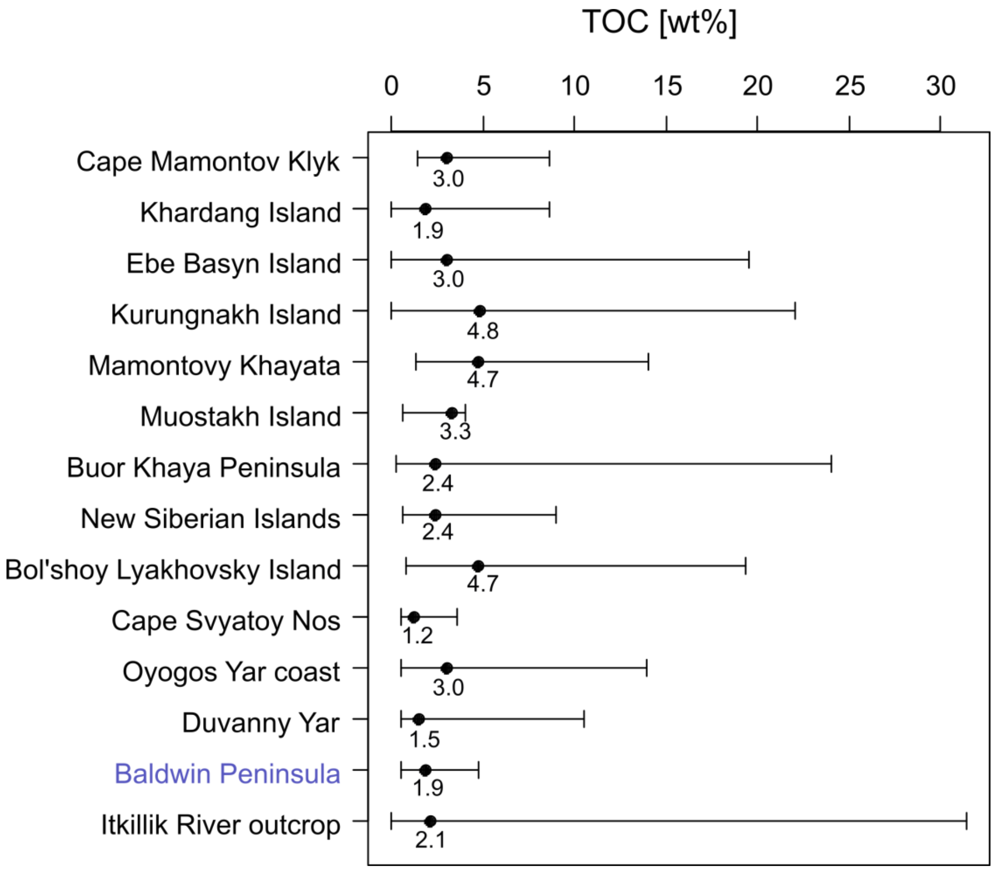

Figure S6: Total organic carbon (TOC) variations from different yedoma study sites in Siberia and Alaska. Sorted from westernmost (Cape Mamontov Klyk, western Laptev Sea) to easternmost (Itkillik River outcrop, Alaskan North Slope) study sites. Data from Schirrmeister et al. (2008a, 2008b, 2011), Strauss et al. (2012, 2013, 2015) and Baldwin Peninsula (this study; blue).

2.3 Additional profiles

Figure S7 shows the cryostratigraphical and biogeochemical parameters of the additional drained thermokarst lake basin exposures BAL16-B3 and BAL16-B5 that were used in the organic carbon calculations.

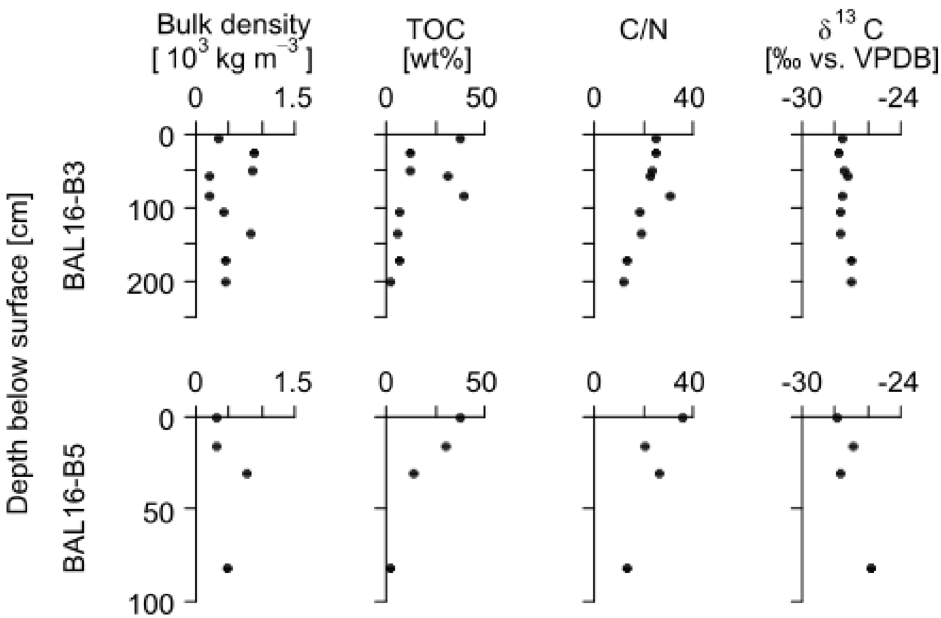

Figure S7: Summary of cryostratigraphical and biogeochemical parameters of BAL16-B3 and BAL16-B5 (drained thermokarst lake basin exposures): bulk density, total organic carbon (TOC), total organic carbon-total nitrogen ratio (C/N), stable carbon isotopes ($\delta^{13}C$).

2.4 *n*-Alkane concentration

The *n*-alkane concentrations per sample are shown in Figure S8. Also, the dominating *n*-C chain is indicated.

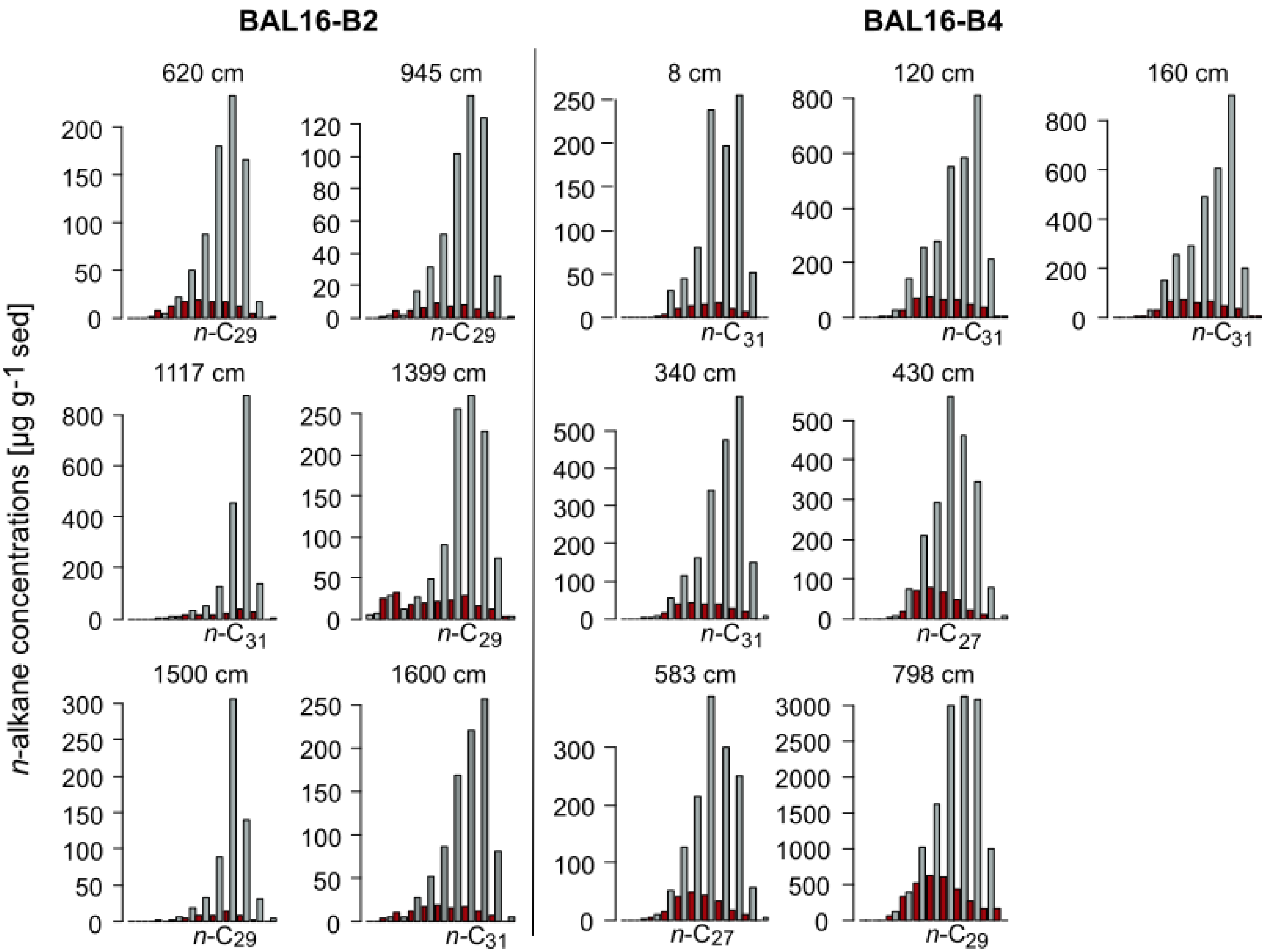

Figure S8: *n*-alkane concentrations of BAL16-B2 (yedoma) and BAL16-B4 (drained thermokarst lake basin) by depth. Odd chains (grey bars) and even chains (red bars), sample depth (above graph) and dominating *n*-chain indicated (below x-axis). Note: different y-axes.

2.5 Depositional environment

2.5.1 Grain size distribution

The grain size distributions of yedoma exposure BAL16-B2 and drained thermokarst lake basin exposure BAL16-B4 are shown in Figure S9 and Figure S10, respectively.

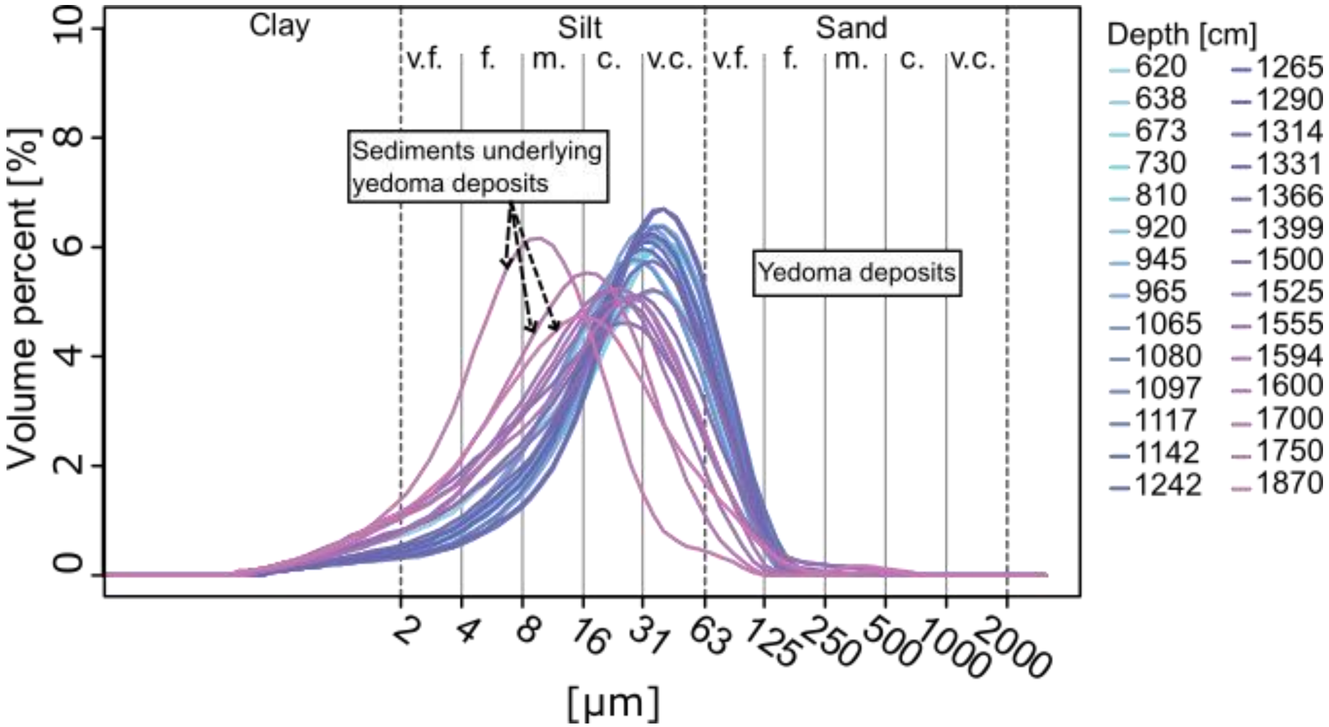

Figure S9: Grain size distribution of BAL16-B2 (yedoma). Samples sorted over depth (legend on the right). v.f.: very fine, f.: fine, m.: medium, c.: coarse, v.c.: very coarse. Sediments from the separate unit underlying the yedoma deposits indicated.

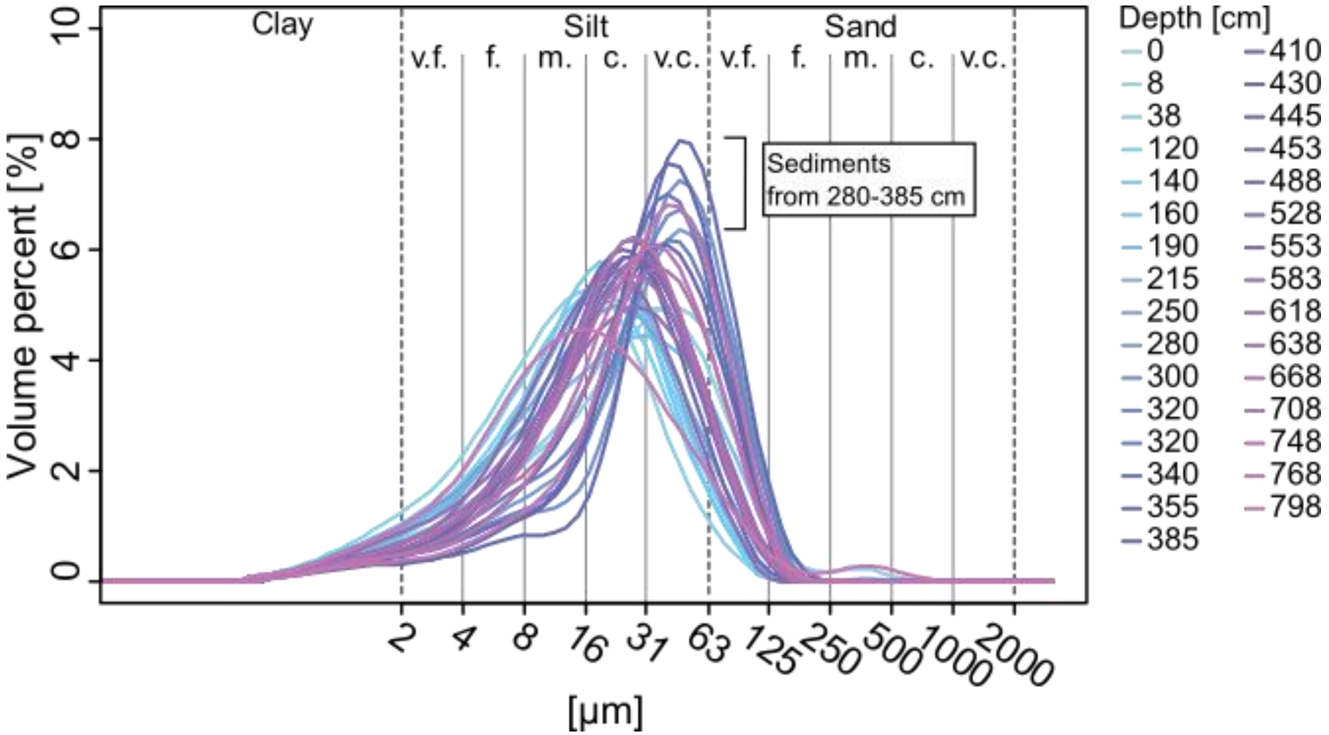

Figure S10: Grain size distribution of BAL16-B4 (drained thermokarst lake basin). Samples sorted over depth (legend on the right). v.f.: very fine, f.: fine, m.: medium, c.: coarse, v.c.: very coarse. Sediments from depth interval of 280-385 cm indicated.

2.5.2 Climatic indicators

Table S1 shows the brGDGT derived climatic indices BIT and MBT indices.

Table S1: brGDGT derived climatic indices for BAL16-B2 (yedoma) and BAL16-B4 (drained thermokarst lake basin): branched and isoprenoid tetraethers (BIT) index and methylation of branched tetraethers (MBT) index.

	Depth [cm]	BIT	MBT
Yedoma	620	0.90	0.19
	945	0.96	0.19
	1117	NA	NA
	1399	1.00	0.39
	1500	0.97	0.20
	1600	0.88	0.18
DTLB	8	1.00	0.25
	120	1.00	0.27
	160	1.00	0.30
	340	0.99	0.25
	430	1.00	0.22
	583	1.00	0.16
	798	NA	NA

2.6 Statistical tests

Using the Shapiro-Wilk test, we tested for normality of the data (Table S2). In this test, the null hypothesis states that the data are normally distributed. When the p-value exceeds 0.05, the null hypothesis cannot be rejected. Using the Kruskal-Wallis test, a non-parametric test, we tested for significant differences of the biogeochemical parameters (bulk density, total organic carbon, carbon-nitrogen ratio and stable carbon isotopes) between the three stratigraphic landscape units on Baldwin Peninsula (Table S2): yedoma, drained thermokarst lake basin and thermokarst lake sediments. In this test, the null hypothesis states that there is no statistically significant difference between the samples of the different landscape units. A Mann-Whitney-Wilcox test was added for pairwise comparisons between the landscape units (Table S2).

The Mann-Whitney-Wilcoxon test was also used to test for significant differences based on the C/N (**Table S3**) and the $\delta^{13}C$ value (Table S4) between this study (Baldwin Peninsula) and other studies from Alaska: yedoma deposits along the Itkillik River (IR) (Lapointe et al., 2017; Strauss et al., 2012), DTLB deposits from the Northern Seward Peninsula (NSP) (Lenz et al., 2016) and thermokarst lake sediments from lakes in the Kobuk River Delta (KOB) and Central Seward Peninsula (CSP) (Lenz et al., 2018).

Table S2: Outcome statistical tests of bulk density (BD), total organic carbon (TOC), carbon-nitrogen (C/N) ratio and stable carbon isotopes ($\delta^{13}C$) between BAL16-B2 (yedoma), BAL16-B4 (drained thermokarst lake basin; DTLB) and BAL16-UPL1-L1 (thermokarst lake) on Baldwin Peninsula.

P-value		BD	TOC	C/N	$\delta^{13}C$
Shapiro-Wilk Test		<0.05	<0.001	<0.01	<0.001
Kruskal Wallis Test		<0.05	<0.001	<0.05	<0.001
Wilcoxon test	Yedoma – DTLB	<0.05	<0.001	<0.001	<0.001
	Yedoma – Thermokarst lake	<0.001	<0.001	<0.001	<0.001
	DTLB – Thermokarst lake	<0.001	<0.001	<0.001	<0.001

Table S3: Outcome Mann-Whitney-Wilcoxon test of C/N ratio between yedoma, drained thermokarst lake basin (DTLB) and thermokarst lake sediments. BP: Baldwin Peninsula (this study), IT: Itkillik River (Strauss et al., 2012), NSP: Northern Seward Peninsula (Lenz et al., 2016), KOB: Kobuk River Delta and CSP: Central Seward Peninsula (Lenz et al., 2018).

P-value C/N	DTLB BAL16-B4	Thermokarst lake BAL16-UPL1-L1	Yedoma Itkillik River	DTLB Northern Seward Peninsula	Thermokarst lake Kobuk Delta	Thermokarst lake Central Seward Peninsula
Yedoma BAL16-B2	<0.001	<0.001	>0.05	<0.001	<0.001	<0.001
DTLB BAL16-B4		<0.01	<0.001	<0.01	>0.05	<0.001
Thermokarst lake BAL16-UPL1-L1			<0.001	<0.001	<0.001	>0.05
Yedoma Itkillik River				<0.001	<0.001	<0.001
DTLB Northern Seward Peninsula					<0.001	<0.001
Thermokarst lake Kobuk Peninsula						<0.01

Table S4: Outcome Mann-Whitney-Wilcoxon test of δ^{13}C between yedoma, drained thermokarst lake basin (DTLB) and thermokarst lake sediments. BP: Baldwin Peninsula (this study), IT: Itkillik River (Strauss et al., 2012), NSP: Northern Seward Peninsula (Lenz et al., 2016), KOB: Kobuk River Delta and CSP: Central Seward Peninsula (Lenz et al., 2018).

P-value δ^{13}C	DTLB BAL16-B4	Thermokarst lake BAL16-UPL1-L1	Yedoma Itkillik River	DTLB Northern Seward Peninsula	Thermokarst lake Kobuk Delta	Thermokarst lake Central Seward Peninsula
Yedoma BAL16-B2	<0.001	<0.001	>0.05	<0.001	<0.001	<0.001
DTLB BAL16-B4		<0.001	<0.001	>0.05	<0.001	<0.001
Thermokarst lake BAL16-UPL1-L2			<0.001	<0.001	<0.01	>0.05
Yedoma Itkillik River				<0.001	<0.001	<0.001
DTLB Northern Seward Peninsula					<0.001	<0.001
Thermokarst lake Kobuk Delta						<0.01

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