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Carbon geochemistry of plankton-dominated supra-micron samples in the Laptev and East Siberian shelves: contrasts in suspended particle composition

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Abstract

Recent Arctic studies suggest that sea-ice decline and permafrost thawing will affect phytoplankton dynamics and stimulate marine heterotrophic communities. However, in what way the plankton composition will change as the warming proceeds remains elusive. Here we investigate the chemical signature and plankton speciation of the supra-micron (> 10 μm) particulate organic matter (supra-POM) fraction collected along the Siberian shelf. Supra-POM samples were analysed at bulk ($\delta^{13}C$ and $\Delta^{14}C$) and molecular level (CuO oxidation and IP_{25}) while plankton identification established the dominant taxa. In addition, surface water chemical properties were integrated with the plankton dataset to understand the link between plankton composition and environmental conditions.

The dual-carbon isotope fingerprint indicates a large variability in the supra-POM distribution while terrestrial biomarkers suggest negligible land-derived input. In the open-waters of the outer Laptev Sea (LS), heterotrophic plankton dominated the assemblages. $\delta^{13}C$ and $\Delta^{14}C$ suggest that modern terrestrial dissolved organic carbon (DOC) from the Lena river is the primary source of metabolizable carbon which is transferred to the heterotrophic communities via microbial loops. Moving eastwards toward the sea-ice dominated East Siberian Sea (ESS), the system became progressively more autotrophic and dominated by sea-ice and pelagic diatoms which is confirmed. Comparison between $\delta^{13}C$ of supra-POM samples and CO_2aq concentrations suggests that the carbon isotope fractionation follows the general growth *vs* CO2aq supply model with the highest $\delta^{13}C$ values found in the easternmost, most productive stations.

In a warming scenario characterized by enhanced terrestrial release and further sea-ice decline, heterotrophic conditions fuelled by terrestrial DOC will likely persist in the LS while

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ESS might experience enhanced primary productivity. This will result in a sharp compositional gradient similar to what documented in our semi-synoptic study.

1. Introduction

The progressive reduction of sea-ice extent in the Arctic Ocean is indisputable evidence of modern global warming (Comiso et al., 2008; Kwok and Rothrock, 2009). The unprecedented decline of sea-ice is expected to alter several aspects of the Arctic marine ecology such as plankton abundance and its temporal distribution (Arrigo et al., 2008). For instance, recent studies suggest that the increase of solar irradiance will stimulate greater primary productivity in summer while the prolonged ice-free conditions will develop a second algal bloom in early fall, which is a distinctive feature of only lower latitudes (Ardyna et al., 2014; Lalande et al., 2009; Lalande et al., 2014). The phytoplankton communities are expected to profoundly change towards a higher contribution from open water phytoplankton at the expense of sea-ice assemblages (Fujiwara et al., 2014). Taken together, a greater productivity in the ice-free or marginal ice zone compare to in the inner multi-year ice system, is also expected to lead to greater uptake and settling export of organic carbon from the surface to deeper strata of the Arctic Ocean (Gustafsson and Andersson, 2012).

Sea-ice decline will also project to water-air gas exchange, currents and river plume dispersion which, in turn, exert large control on the surface water chemical/physical properties (Aagaard and Carmack, 1989; Ardyna et al., 2014; Lalande et al., 2014). On top of this, destabilization of several aspects of permafrost and hydrology on land will results in enhanced particulate and dissolved carbon input to the Arctic Ocean (Frey and Smith, 2005; Vonk et al., 2012). Thus, the geochemical signature of both autotrophic and heterotrophic plankton communities is also expected to change as the warming proceeds. However, how the cryosphere destabilization will ultimately affect the marine geochemical signal is poorly

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understood. This study seeks a better understanding of the chemical composition of plankton that dominates regions of the Arctic Ocean characterized by different sea-ice coverages and terrestrial input. In particular, we focus on the carbon isotope fingerprint (i.e., $\delta^{13}C$ and $\Delta^{14}C$) of plankton that grows in ice-covered and ice-free Marginal Ice Zone (MIZ) regimes in the river-dominated Siberian margin. The motivation behind investigating the chemical fingerprint of plankton from different sea-ice domains is to provide a better understanding of the carbon signature for direct applications to carbon studies of both modern systems and paleo-reconstructions. In particular, the isotope composition of marine OC finds several applications in climate, ecology and carbon source apportionment studies. For example, stable carbon isotopes of marine phytoplankton are used for paleo-pCO_2 reconstructions over geological time scales (Hoins et al., 2015; Pagani et al., 1999; Popp et al., 1999; Rau, 1994). The $\delta^{13}C$ signature also provides a solid tool for marine food web and ecosystem structure investigations (Dunton et al., 2006; Iken et al., 2005; Kohlbach et al., 2016). Furthermore, dual-carbon isotope mixing models ($\delta^{13}C$ and $\Delta^{14}C$) are commonly used to quantify the relative proportion of marine and various allocthonous sources (e.g., permafrost soil) in both contemporary and paleo-reconstructed carbon cycling of the Arctic (Karlsson et al., 2016; Tesi et al., 2016; Vonk et al., 2012; Vonk et al., 2014).

With this overarching goal in mind, here we investigate the >10 μm (supra-micron) fraction of particulate organic matter (supra-POM) in ice-covered and ice-free MIZ regimes of the Siberian Arctic Shelf during the SWERUS-C3 expedition (July-August 2014) (Fig. 1). The plankton-dominated supraPOC samples collected throughout the ca. 4,500 km long cruise track were characterized at bulk (OC, $\delta^{13}C$ and $\Delta^{14}C$) and biomarker level (highly branched isoprenoids, IP_{25}; CuO oxidation products) while plankton identification via microscope provided information about the dominant assemblages. In addition, continuous measurements of dissolved CO_2 (CO_{2aq}) and its stable carbon isotope composition ($\delta^{13}C_{CO2}$) were performed

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during the campaign for a direct comparison with the chemical composition of the supra-POM fraction.

2. Methods

2.1 Supra-micron fraction sampling

Seawater was pumped from a stainless steel inlet on the hull of the icebreaker *Oden* positioned at 8 m below the sea surface. The inlet system is tested and further described in Sobek and Gustafsson (2004) and Gustafsson et al. (2005). Figure 1a shows the region covered to harvest each supra-POM samples. The particulate material was retained via a large volume filtration apparatus using a 10-μm Nitex® (nylon) mesh placed in a 29.3 cm filter holder. After collection, filtered samples were rinsed with MilliQ water and the particulate material (i.e., supra-micron fraction) was kept frozen throughout the expedition. In the lab, samples were transferred in pre-cleaned Falcon® tubes and centrifuged to remove the supernatant. The residual particulate material was frozen and subsequently freeze-dried prior to biogeochemical analyses.

In all figures, sample location of the supra-POM samples refers to its time-averaged position as shown in Figure 1.

2.2 Bulk carbon isotopes and biomarker analyses

Organic carbon (OC) and stable carbon isotope ($\delta^{13}C$) analyses were carried out on acidified samples (Ag capsules, HCl, 1.5M) to remove the carbonate fraction (Nieuwenhuize et al., 1994). Analyses were performed using a Thermo Electron mass spectrometer directly coupled to a Carlo Erba NC2500 Elemental Analyzer via a Conflo III (Department of Geological Sciences, Stockholm University). OC values are reported as weight percent (%d.w.) whereas stable isotope data are reported in the conventional $\delta^{13}C$ notation (‰). The

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analytical error for $\delta^{13}C$ was lower than ±0.1‰ based on replicates. Acidified (HCl, 1.5 M) samples for radiocarbon abundance were analysed at the US-NSF National Ocean Science Accelerator Mass Spectrometry (NOSAMS) facility (Woods Hole Oceanographic Institution, Woods Hole, USA). Radiocarbon data are reported in the standard $\Delta^{14}C$ notation (‰).

Alkaline CuO oxidations were carried out using an UltraWAVE Milestone microwave as described in Tesi et al. (2014). Briefly, about 2 mg of OC was oxidised using CuO under alkaline (2N NaOH) and oxygen-free conditions at 150 °C for 90 min in teflon tubes. After the oxidation, known amounts of recovery standards (trans-cinnamic acid and ethylvanillin) were added to the solution. The NaOH solutions were then acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. Extracts were dried and redissolved in pyridine. CuO oxidation products were quantified by GC-MS in full scan mode (50-650 m/z). Before GC analyses, the CuO oxidation products were derivatized with bis(trimethylsilyl) trifluoroacetamide+1% trimethylchlorosilane at 60°C for 30 min. The compounds were separated chromatographically in a 30m×250 µm DB5ms (0.25 µm thick film) capillary GC column, using an initial temperature of 100°C, a temperature ramp of 4°C/min and a final temperature of 300°C. Lignin phenols (terrestrial biomarkers) were quantified using the response factors of commercially available standards (Sigma-Aldrich) whereas the rest of the CuO oxidation products were quantified by comparing the response factor of trans-cinnamic acid. Lignin-derived reaction products include vanillyl phenols (V=vanillin, acetovanillone, vanillic acid), syringyl phenols (S=syringealdehyde, acetosyringone, syringic acid) and cinnamyl phenols (C=p-coumaric acid, ferulic acid). In addition to lignin, cutin-derived products (hydroxyl fatty acids) were used to trace the land-derived input (Goñi and Hedges, 1990; Tesi et al., 2010). Other CuO oxidation products include para-hydroxybenzene monomers (P-series), benzoic acids (B-series) and short-chain fatty acids (FA-series) which can have both terrestrial and marine origin (Goñi and Hedges, 1995; Tesi et al., 2010).

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IP_{25} (monounsaturated highly branched isoprenoid) was quantified according to Belt et al. (2012). Briefly, lipids were extracted via sonication using a dichloromethane/methanol solution (2:1 v/v × 3). Prior to the extraction, two internal standards (7-hexylnonadecane, 7-HND and 9- octylheptadecene, 9-OHD) were added to permit quantification of IP_{25} (monounsaturated highly branched isoprenoid) following analysis via GC-MS. Total lipid extracts (TLEs) were dried under N_2 after removing the water excess with anhydrous $NaSO_4$. Dry TLEs were redissolved in dichloromethane and the non-polar hydrocarbon fraction was purified using open column chromatography (activated SiO_2) and hexane as eluent. Saturated and unsaturated n-alkanes were further separated using 10% $AgNO_3$ coated silica gel using hexane and dichloromethane, respectively.

Quantification of IP_{25} was carried out in SIM mode (*m/z* 350.3) as described in Belt et al. (2012). The GC was fitted with a 30m×250 µm DB5ms (0.25 µm thick film) capillary GC column. Initial GC oven temperature was set to 60°C followed by a 10°C/min ramp until a final temperature of 310°C (hold time 10 min).

2.3. Microscope images of plankton

High resolution digital images were taken with an Environmental Scanning Electron Microscope (ESEM) Philips XL30 FEG in high voltage (15kV) and magnification 250X. Samples were further studied for identification of diatoms and dinoflagellates using a transmitted light microscope (Leitz Laborlux 12 Pol) equipped with differential interference contrast optics at 1000X magnification.

2.4 WEGAS measurements of CO_2aq

Cavity ring-down spectrometer (CRDS) measurements were used to continuously monitor CO_2 concentrations and $\delta^{13}C_{CO2}$ composition of gas stripped via headspace

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equilibration from the water column using the Water Equilibration Gas Analyser System (WEGAS) (Thornton et al. 2016). It consists of three major components:

a) Water handling system including i) showerhead equilibrator (head space volume 1 L) fed by the sea water intake described above, ii) continuous pH measurements by E&H electrode probe and iii) T and salinity measurements by Seabird TSG 45.

b) CRDS gas analyzers for CO_2 stable carbon isotopes (model G2131-i, Picarro Inc., Sunnyvale, CA) and CO_2 concentrations (model G2301, Picarro Inc., Sunnyvale, CA).

c) Gas handling system with circulation pumps for headspace and ambient air from meteorological tower.

Continuous measurements of surface water CO_2 and $\delta^{13}C_{CO2}$, were thus performed using IB/Oden's seawater intake. Water was pumped through spray nozzles into the open headspace equilibrator at ~4.5 L min^{-1}. By creating a fine spray of droplets, the exchange surface between headspace and water is maximized and an optimal equilibration is achieved. The gas of the headspace was analysed using two different CRDS (cavity ring-down) analysers. The second analyser was operated in parallel and its flow (~25 mL min^{-1}) was not fed back into the closed cycle. Thus, it created a defined vent flow. This vent flow is compensated by a flow of ambient air (AA) taken from the top inlet of the meteorological tower (20 m height). To be able to correct the data for the vent flow, the concentration of CO_2 and $\delta^{13}C_{CO2}$ in AA is monitored by frequent switching. During the SWERUS-C3 expedition, continuous CO_2 and $\delta^{13}C$-CO_2 measurements in the surface waters have been performed in the period 10 July - 9 August resulting in a total of 238 864 data points.

For this study all measurement data taken within a time window of +/-5min around the specific start times of the sample taking were averaged to account for filling time of the canister and residence time of the water in the SWI.

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200 **2.5 Sea-ice data**

201 Daily AMSR2 sea-ice extent and concentration maps were provided by the Institute of
202 Environmental Physics, University of Bremen, Germany (Spreen et al., 2008) as GeoTIFF
203 files (ftp://seaice.uni-bremen.de).

204

205 **3. Results and discussion**

206 **3.1 Surface water conditions**

207 Before discussing the chemical composition of the supra-POM fraction, here we
208 briefly introduce the different environmental conditions encountered throughout the cruise
209 track. The surface water data presented in this section were pulled together from previous
210 studies which provide an in-depth analysis of the surface water properties during the
211 SWERUS-C3 expedition (Humborg et al., submitted; Salvadó et al., 2016; The SWERUS-C3
212 Scientific Party, 2016) (Table 2). For this study, continuous CO_2aq and $\delta^{13}C_{CO2}$ data
213 (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) acquired throughout the
214 expedition were organized to match the water sampling stations allowing for a direct
215 comparison with DOC and salinity data (Fig. 2).

216 Summer 2014 was consistent with the long-term downward trend in Arctic sea-ice
217 extent. The strongest anomalies were observed in the LS which experienced the most
218 northerly sea-ice shift since satellite observations began in 1979. In general, sea-ice displayed
219 a strong gradient over the study region going from ice-free conditions in the outer LS to ice-
220 dominated waters in the outer ESS. Figure 1 displays sea-ice extent and concentration at the
221 beginning, in the middle and at the end of the sampling. Furthermore, Table 1 reports the
222 averaged sea-ice concentrations for each sample.

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The surface water salinity exhibited a longitudinal trend characterized by low values in the outer LS while the sea-ice dominated ESS waters showed relatively higher values (Fig. 2a; Table 2). However, the highest salinity values were measured in the westernmost stations resulting in a sharp gradient in the LS. The low surface water salinities in the outer LS are most likely the result of both Lena river input and sea-ice thawing (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) that started in late May (Janout et al., 2016).

The highest DOC concentrations were measured in the mid-outer LS in the surface water plume affected by Lena River runoff (Fig.2b; Table 2). Overall, DOC concentrations mirrored the salinity distribution with high DOC concentrations corresponding to low salinities (Fig. 2). Carbon stable isotopes ($\delta^{13}C$) and terrestrial biomarkers (of the solid-phase extracted DOC fraction; Salvado et al., 2016) further confirmed the influence of terrestrial DOC in the outer LS, while the terrestrial imprint decreased moving eastward.

CO_2aq concentrations exhibited a typical estuarine pattern over the study region (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) (Fig. 2d; Table 2). Low salinity waters in the outer LS showed above atmospheric CO_2 concentrations (i.e., oversaturation) while surface waters below sea-ice exhibited undersaturated concentrations. The most depleted $\delta^{13}C_{CO2}$ values were measured off the Lena river mouth (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) (Fig. 2e; Table 2). Being relatively rich in land-derived material, it is likely that respired terrestrial OC within the river plume exerted control on the CO_2 isotopic signature and concentration.

Finally, nutrient distribution revealed nitrate (NO_3) and nitrite (NO_2) depletion in surface waters throughout the cruise track (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016). Phosphate (PO_4) exhibited rather low concentrations in the outer LS and relatively higher concentrations below the sea-ice in the outer ESS (Humborg et al.,

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submitted; The SWERUS-C3 Scientific Party, 2016) likely reflecting the Pacific inflow (Semiletov et al., 2005).

3.2 Source of the supra-micron POM fraction

The Arctic Ocean off northern Siberia receives large quantities of dissolved and particulate terrestrial organic carbon (TerrOC) via continental runoff and coastal erosion (Alling et al., 2010; Dittmar and Kattner, 2003; McClelland et al., 2016; Sánchez-García et al., 2011; Semiletov et al., 2013; Vonk et al., 2012). The land-derived material that does not settle in the coastal zone further travels across the margin reaching out to the outer-shelf region resuspended within the benthic nepheloid layer or in suspension within the surface river plume (Fichot et al., 2013; Sánchez-García et al., 2011; Wegner et al., 2003). Thus, we addressed to what extent TerrOC affects the supra-POM fraction by quantifying the concentration of lignin phenols and C16-18 hydroxy fatty acids (cutin-derived products). These biomarkers are exclusively formed by terrestrial vegetation and, thus, serve as tracers of TerrOC in the marine Arctic environment (Amon et al., 2012; Bröder et al., 2016b; Feng et al., 2015).

Upon CuO alkaline oxidation the supra-POM samples yielded only traces of lignin phenols while the cutin-derived products were not detected (Fig. 3). Other oxidation products in high abundance included saturated and mono-unsaturated short chain fatty acids (C12-18FA), para-hydroxy phenols, benzoic acids and dicarboxylic acids. These other reaction products are ubiquitous in both marine and terrestrial environments but they are predominant in plankton-derived material, especially short-chain fatty acids . When compared with active-layer permafrost soils and ice-complex deposits (Tesi et al., 2014), supra-POM samples displayed a distinct CuO fingerprint dominated by short chain fatty acids (Fig. 3), consistent with the typical CuO fingerprints of phytoplankton batch cultures (Goñi and Hedges, 1995).

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SEM images further corroborated the abundance of marine plankton detritus in the supra-POM fraction while lithogenic particles (clastic material) appeared to be sporadic in all samples.

The OC content (% d.w.) of the supra-POM fraction decreased eastwards showing high concentrations in the LS and relatively low values in the ESS (Table 1). However, in terms of absolute concentration in the water column (µC/l), the highest levels were generally observed in the sea-ice covered region (Table 1; Fig. 4a). Qualitative analyses by SEM and transmitted-light microscopy highlight important differences in plankton assemblages which reflect different timing of the plankton blooms which can explain these differences in concentration. Specifically, the open-water LS stations exhibited a low degree of plankton diversity and were largely dominated by a bloom of heterotrophic dinoflagellate cysts (*Protoperidinium* spp) (Fig. 5a; Table 3). Moving towards the ice-dominated regions, diatoms become the prevailing species. Dominant diatom genera include *Chaetoceros spp.* (dominant diatom in several stations), *Thalassiosira spp.*, *Rhizosolenia spp.*, *Coscinodiscus spp.*, *Asteromphalus spp.*, *Navicula spp.* as well as sea-ice species such as *Fragilariopsis cylindrus* and *Fragilariopsis oceanica* (Fig. 5b,c; Table 3).

A moored line deployed in the LS shelf recorded the sea-ice retreat in 2014 and found no sign of pelagic under-ice blooms despite available nutrients while high chlorophyll concentrations were detected immediately after the ice retreated in late May (Janout et al., 2016). The ice-edge blooms lasted for about 2 weeks according to the high resolution chlorophyll time-series (Janout et al., 2016). Thus, our post-bloom sampling in the LS essentially captured an oligotrophic environment (Gustafsson et al., 2016) dominated by heterotrophic dinoflagellate cysts (i.e, Protoperidinium spp) which likely fed on phytodetritus and river-derived organic material. Such conditions are fairly consistent with the relatively low carbon contents observed in LS waters (Fig. 4a).

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297 The Arctic sea-ice biomarker IP25 (Fig. 4b) further corroborated the sampling of
298 different plankton taxa in ice-free and ice-dominated surface waters. IP25 is a proxy of sea-ice
299 based on a highly branched mono-unsaturated isoprenoid alkene found in some sea-ice
300 diatoms which, however, generally account for 5% of the total sea-ice taxa (Belt et al., 2007;
301 Brown et al., 2014). The IP25 concentrations varied by several orders of magnitude over the
302 study area showing low concentrations in the open-water western region while the sea-ice
303 dominated surface waters to the east exhibited high concentrations especially at station 31b
304 (Fig. 4b; Table 1). The fact that IP25 was still detectable throughout the ice-free outer LS
305 suggests that the proxy captured the signal of the sea-ice retreat that occurred shortly before
306 the sampling at the end of May/early June (Janout et al., 2016).
307
308 **3.3. $\delta^{13}C$ and $\Delta^{14}C$ of the supra-micron POM fraction**
309 $\delta^{13}C$ and $\Delta^{14}C$ of the supra-POM fraction also exhibited a distinctive longitudinal
310 trend across the study area (Fig. 4c,d).
311 Depleted $\delta^{13}C$ values characterized the LS open waters ranging from -28.1 to -24.7‰
312 (Fig. 4c). Although within the range of terrestrially-derived material, our CuO oxidation data
313 (i.e. trace of lignin phenols and absence of cutin-derived products) suggest that the "light"
314 isotopic composition in the LS might instead reflect the plankton assemblage dominated by
315 heterotrophic dinoflagellate cysts as previously described (e.g., *Protoperidinium* spp; Fig. 5a).
316 More specifically, heterotrophic dinoflagellates can adapt their metabolism depending on the
317 substrate available (e.g., diatoms and bacteria). Several studies have shown that terrestrial
318 DOC greatly promotes bacteria biomass production which in turn stimulates the growth of
319 heterotrophic dinoflagellates (Carlsson et al., 1995; Purina et al., 2004; Wikner and
320 Andersson, 2012). Thus, in these conditions, allochthonous terrestrial DOC is actively

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recycled by bacteria and transferred to dinoflagellates which explains, thus, the depleted $\delta^{13}C$ values observed in the river-dominated samples (Carlsson et al., 1995).

The modern radiocarbon fingerprint of the Lena DOC discharge is consistent with $\Delta^{14}C$ signature of the supra-POM fraction in the LS (up to +99 ‰), supporting, thus, the DOC microbial loop within the river plume (Fig. 4d and 6). By contrast, comparison with other potential carbon sources which include the Lena river particulate organic carbon, surface sediments, Pleistocene coastal Ice-Complex Deposit and Pacific DIC inflow reveals a different (more depleted) radiocarbon fingerprint (Fig. 6).

Moving towards the ice-dominated ESS, surface waters progressively become more autotrophic and productive (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) while the supra-POM exhibited a wide $\delta^{13}C$ signature ranging from -28.6 to -21.2‰ (Fig. 4c). The most depleted values were observed across the transition zone between open-waters and sea-ice. Visual inspections of these samples revealed large abundance of the centric diatom *Chaetoceros* spp. (spores and vegetative cells; St22, Fig. 5b) while lignin and cutin data indicated, a negligible input of land-derived material. Primary factors determining the fractionation of stable carbon isotopes in phytoplankton are several and include CO_2aq concentration, $\delta^{13}Caq$, growth rate, cell size, cell shape, light and nutrient availability (Gervais and Riebesell, 2001; Laws et al., 1997a; Popp et al., 1998; Rau et al., 1996). Our understanding about isotopic fractionation has been historically achieved via laboratory experiments designed to test each factor under controlled conditions. In natural environments, however, different factors can compete with each other, sometimes in opposite directions. Yet, the existing knowledge about surface water properties during the expedition (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) can provide important constraints for the isotopic signal interpretation.

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For example, comparison with continuous $\delta^{13}C$-CO_2aq and CO_2aq data measured throughout the cruise track - time-averaged to match the large volume filtration along the cruise track (Table 1) - suggested a negligible role exerted by $\delta^{13}C$-CO_2aq (Fig. 7b) while CO_2aq concentration correlated with the $\delta^{13}C$ of the supra-POM fraction (r^2=0.72) (Fig. 7a). Such a relationship fits with the general model according to which a low demand (i.e., low growth rate) and high supply (i.e., abundant CO_2aq) favour high fractionation and vice versa (Laws et al., 1997b; Laws et al., 1995; Wolf-Gladrow et al., 1999).

During the expedition, surface water properties (i.e. O_2 and CO_2, Table 2) (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016) suggest that the productivity in the outer ESS increases moving eastward, as commonly observed, likely due to the Pacific inflow (Björk et al., 2011; Semiletov et al., 2005). Thus, the wide range of plankton $\delta^{13}C$ over the ESS can be explained in terms of two different regimes: (a) in the transition zone between open waters and sea-ice, the productivity was low but CO_2aq was oversaturated while (b) in the easternmost ESS, productivity was high but CO_2aq was depleted (Fig. 7b). The former regime favours fractionation while the latter does not (Fig. 7b). Different diatom assemblages can also be another factor to consider although the phytoplankton diversity observed over ESS can be considered rather small (e.g. *Chaetoceros spp.* dominant in most of the samples) compared to the wide range of $\delta^{13}C$ observed (i.e., from -28.8 to -21.6) (Table 3).

The supra-POM fraction in the sea-ice dominated ESS exhibited slightly - but consistently - depleted $\Delta^{14}C$ values ranging from -62 to -49 ‰ (Fig. 4d). This region is affected by the inflow of Pacific waters whose DIC exhibits, however, a modern $\Delta^{14}C$ signature (Griffith et al., 2012) (Fig. 6). By contrast, these results suggest the influence from an aged carbon pool. As the ESS remains covered by sea-ice for most of the year, it is possible that the sea-ice hampers the gas exchange with the atmosphere and acts as a lid by trapping CO_2 which derives from the breakdown of sedimentary organic material (Anderson

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et al., 2009; Semiletov et al., 2016), which might have such ages (Bröder et al., 2016a; Vonk et al., 2012). In these conditions, the pre-aged CO_2 accumulates underneath the sea-ice and is subsequently incorporated during carbon fixation by the phytoplankton. While oversaturated bottom waters were extensively documented in the region with important consequences on the local DIC (Anderson et al., 2009; Pipko et al., 2009), more work is clearly needed to understand if early diagenesis in sediments can also affect the radiocarbon signature of the CO_2aq underneath the sea-ice. Alternatively, the slightly depleted radiocarbon signature might indicate the presence of pre-aged terrestrial organic carbon (Fig. 6) in the supra-POM samples, not reflected in the lignin and cutin tracers (Fig. 3). However, it would then remain elusive why such an aged land-derived influence was not visible in the river-dominated LS waters while it affected the sea-ice dominated region.

Taken together, our results indicate that the dual-carbon isotope fingerprint is highly affected by the trophic conditions (heterotrophic *vs* autotrophic) as well as the extent of primary productivity. In a warming scenario characterized by sea-ice retreat (Arrigo et al., 2008; Comiso et al., 2008) and enhanced terrestrial input from land as result of hydrology and permafrost destabilization (Frey and Smith, 2005; Vonk et al., 2012), the geochemical composition of plankton will likely change as the warming proceeds.

Conclusions

Analyses of large-volume filtrations of plankton-dominated >10 μm particle samples revealed a high degree of heterogeneity in geochemical and plankton composition with an in between ice-free. Thus, the dual-carbon isotope fingerprint of the plankton-dominated fraction reflects a contemporary terrestrial DOC signature (i.e., depleted $\delta^{13}C$ and modern $\Delta^{14}C$ fingerprint). Heterotrophic dinoflagellates dominated the plankton assemblages in this ice-free region. Hence, results suggest a heterotrophic environment in the outer LS open waters where

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395 the river-derived DOC is transferred to relatively higher trophic levels via microbial
396 incorporation (i.e, microbial loop).

397 Moving eastwards towards the ice-dominated outer ESS, surface waters became
398 progressively more autotrophic and largely dominated by diatoms. Here, the isotopic
399 fractionation appears to follow the growth *vs* CO_2 demand model according to which carbon
400 fractionation increases at low growth and high CO_2 supply. As a result, the transition between
401 open-waters and sea-ice exhibited more depleted $\delta^{13}C$ values compared to the productive
402 easternmost stations. Radiocarbon signatures were slightly depleted over the whole sea-ice
403 dominated area. This raises the question whether the sea-ice hampers the gas exchange with
404 the atmosphere and trap the CO_2 sourced from reactive sedimentary carbon pools.

405 In a warming scenario, it is likely that the oligotrophic ice-free LS will be dominated
406 by heterotrophic metabolism fuelled by terrestrially-derived organic material (i.e., Lena
407 input). In these conditions, the dual-carbon isotope signature of the heterotrophic plankton
408 will essentially reflect the terrestrial input. In the ESS, which receives the inflow of the
409 nutrient-rich Pacific waters, ice-free conditions will promote the light penetration. This in turn
410 might further stimulate phytoplankton growth with important implications in terms of CO_2
411 depletion and resulting low isotope fractionation. It is likely that this will result in a sharp
412 compositional gradient (e.g. $\delta^{13}C$) between LS and ESS similar to what has already been
413 captured in our semi-synoptic study.

414

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Table 1. Supra-micron POM (supraPOM) composition and continuous CO_2aq measurements

ID	Time averaged latitude (N)	Time averaged longitude (E)	Mean sea-ice percentage (%)	Supra-micron POM concentration (mg/l)	OC (d.w.)	TN (d.w.)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	IP25 (ng/gOC)	averege CO_2aq (ppm)	average $\delta^{13}C$-CO_2aq (‰)
ST4	81.68	105.96	98.4	6	18.2	3.3	-26.7	n.d.	n.d.	323	-10.9
ST5	80.47	114.07	98.7	15	42.6	3.5	-27.6	n.d.	n.d.	322	-11.0
ST6	78.86	125.22	82.2	1	51.7	3.3	-26.6	99	n.d.	325	-10.8
ST7	77.88	126.62	0.0	11	43.1	2.5	-25.7	n.d.	88	350	-10.7
ST8	77.16	127.32	0.0	17	30.9	2.9	-26.7	41	n.d.	391	-10.5
ST9	76.78	125.83	0.0	3	31.5	3.7	-27.9	30	48	385	-10.5
ST10	76.90	127.81	0.0	11	40.9	2.3	-24.7	n.d.	n.d.	349	-11.0
ST11	77.12	126.66	0.0	13	29.6	2.9	-28.1	27	13	428	-10.7
ST22	77.67	144.63	0.0	20	11.3	1.1	-28.8	n.d.	95	394	-11.0
ST23	76.43	147.53	0.0	6	7.6	0.9	-28.5	-50	n.d.	394	-11.2
ST24	76.42	149.84	34.4	19	11.9	1.3	-26.8	-62	368	374	-11.1
ST25	76.62	152.03	96.7	23	19.5	1.5	-25.7	-31	465	263	-10.8
ST26	76.14	157.85	96.2	109	30.8	1.2	-24.2	-30	217	316	-10.9
ST27	75.00	161.03	91.5	41	23.3	1.4	-23.0	n.d.	256	299	-11.1
ST28	74.63	161.98	86.3	28	15.5	1.5	-23.8	n.d.	n.d.	214	-11.3
ST29	73.61	169.72	79.3	31	14.7	1.3	-23.2	-50	518	184	-11.3
ST30	75.61	174.01	66.7	43	22.6	2.6	-27.0	n.d.	n.d.	304	-10.5
ST31A	75.85	174.41	75.6	30	10.9	1.1	-21.6	-62	1911	182	-10.6
ST31B	74.26	173.74	63.5	15	4.6	0.6	-23.3	n.d.	783	n.d.	n.d.
ST32	73.56	176.06	51.8	21	11.3	1.3	-24.5	-58	131	n.d.	n.d.
ST33	72.35	-175.14	0.0	20	15.5	2.1	-23.5	n.d.	473	n.d.	n.d.
ST34	73.28	-173.05	28.7	76	13.4	1.6	-21.6	-52	970	n.d.	n.d.
ST35	75.21	-172.05	53.9	24	14.3	1.4	-24.2	n.d.	268	n.d.	n.d.

n.d = not determined

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Table 2. Surface water (0-20 m) chemical and physical properties during the SWERUS-C3 expedition*

	Salinity	Temperature	DIC	DOC	POC	δ^{13}C-DIC	NO_2-NO_3	PO_4	O_2
		°C	µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}	‰	µmol kg^{-1}	µmol kg^{-1}	µmol kg^{-1}
	median	**median**	**median**	**median**	**median**	**median**	**median**	**median**	**median**
Outer LS shelf (0-20 m)	32.87	3.84	2139	149.1	7.9	0.75	0.21	0.27	323.0
LS shelf break (0-20 m)	33.56	0.57	2114	91.5	10.1	1.10	0.26	0.15	364.9
Outer ESS shelf (0-20 m)	29.45	-1.33	1969	84.2	10.7	1.14	0.25	0.97	381.5
ESS shelf break (0-20 m)	28.23	-1.32	1979	73.7	4.6	1.47	0.11	0.59	394.1
	mean	**mean**	**mean**	**mean**	**mean**	**mean**	**mean**	**mean**	**mean**
Outer LS shelf (0-20 m)	31.17	3.40	2119	179.8	7.9	0.58	0.60	0.29	327.0
LS shelf break (0-20 m)	33.42	0.96	2111	97.5	10.0	1.10	0.61	0.16	358.1
Outer ESS shelf (0-20 m)	28.95	-0.05	1949	95.8	11.9	1.26	0.26	0.95	386.8
ESS shelf break (0-20 m)	28.27	-1.31	1975	72.0	4.6	1.49	0.12	0.60	397.0
	s.d.	**s.d.**	**s.d.**	**s.d.**	**s.d.**	**s.d.**	**s.d.**	**s.d.**	**s.d.**
Outer LS shelf (0-20 m)	3.22	2.38	89	66.3	1.7	0.50	0.91	0.11	14.6
LS shelf break (0-20 m)	0.70	2.07	23	21.2	1.7	0.11	0.74	0.06	22.5
Outer ESS shelf (0-20 m)	1.41	2.28	75	30.2	4.6	0.49	0.12	0.19	32.2
ESS shelf break (0-20 m)	0.53	0.04	49	3.2	0.3	0.08	0.03	0.02	8.3

*data from (Humborg et al., submitted; The SWERUS-C3 Scientific Party, 2016)

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Table 3. Qualitative plankton characterization of selected supra-micron POC samples

ID	Region	Diatoms	Dinoflagellates	Other species
ST6	LS	Few *Coscinodiscus*	None observed	
ST9	LS	None observed	Few *Protoperidinium*	
ST11	LS	None observed	Abundant *Protoperidinium*	
ST22	LS-ESS	Abundant *Chaetoceros*, few *Rhizosolenia*, *Thalassiosira*	None observed	
ST25	LS-ESS	High diversity. Abundant *Chaetoceros, few Rhizosolenia, Coscinodiscus, Thallasiosira, Asteromphalus, Navicula*	None observed	Silicoflagellate
ST31A	ESS	High diversity. Abundant *Chaetoceros, few Rhizosolenia, Thallasiosira, Bacterosira, Navicula*	None observed	
ST31B	ESS	High diversity. Few *Chaetoceros, Thallasiosira, Fragilariopsis*	Few *Protoperidinium*	
ST34	ESS	Abundant *Chaetoceros*, few *Thalassiosira*, *Navicula*	Few *Protoperidinium*	

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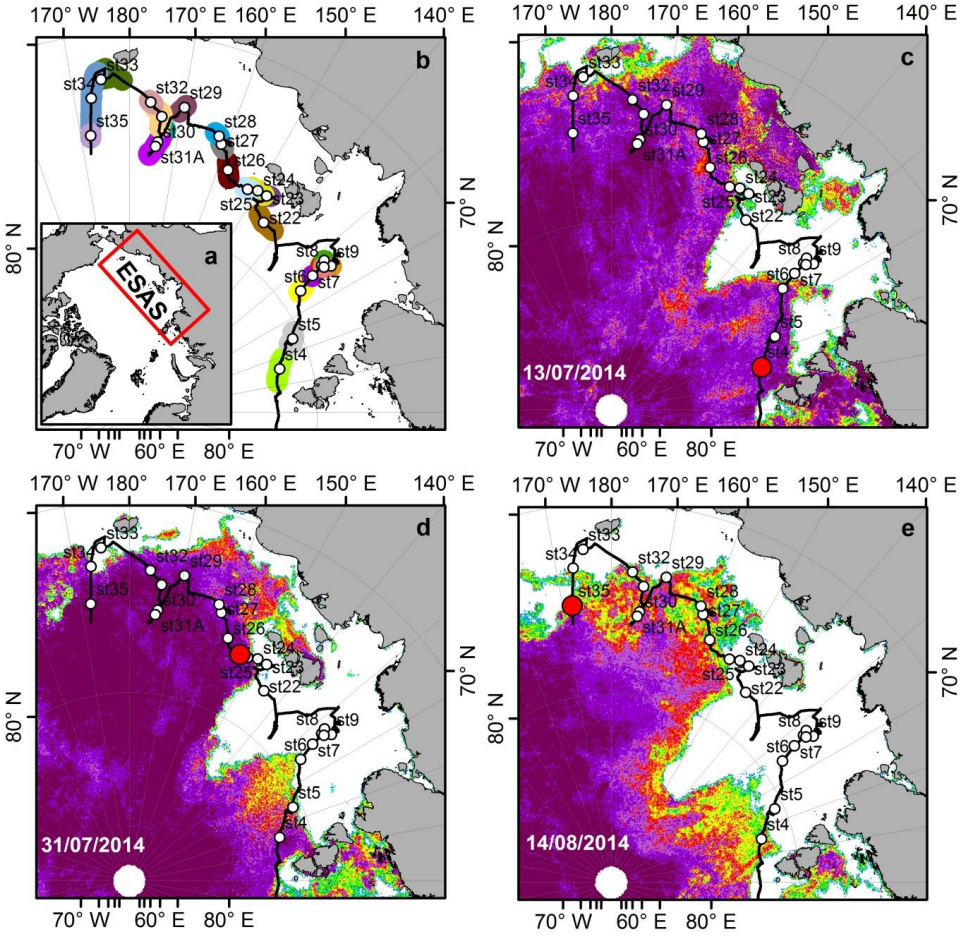

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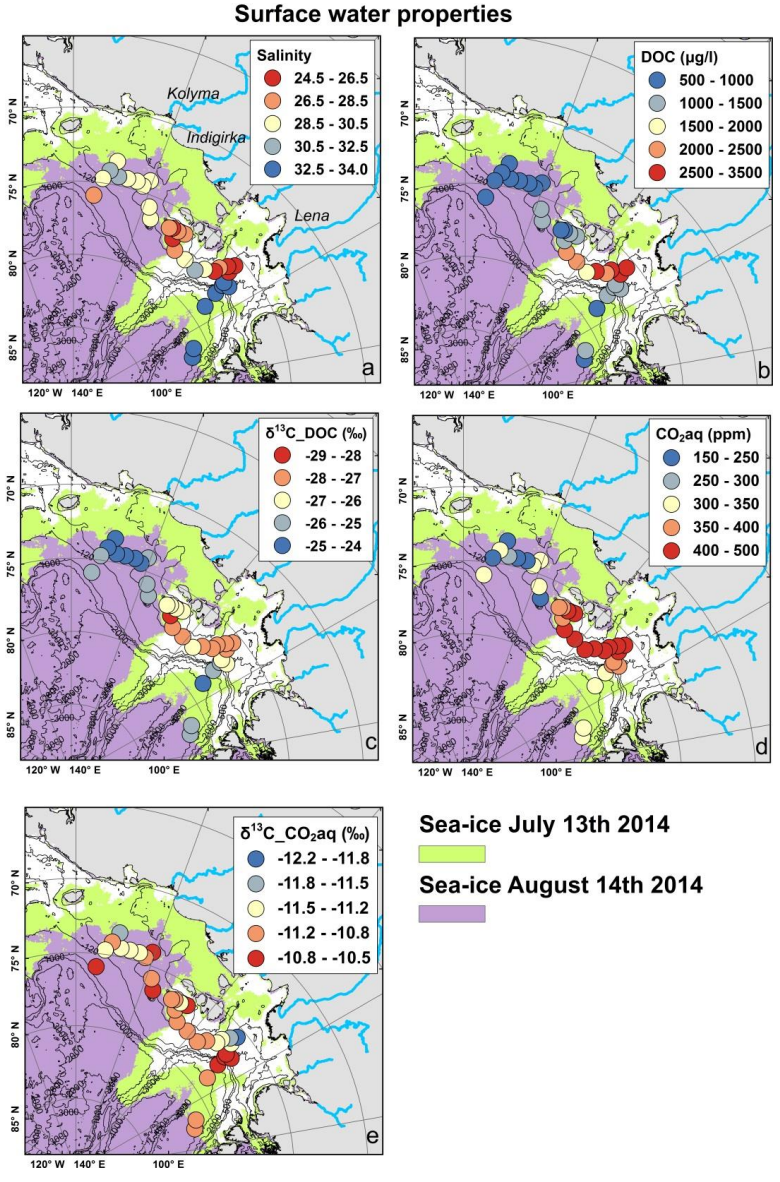
492 **Fig. 1** (a) The study area in the East Siberian Arctic Shelf. (b) Time-averaged position during
493 the large-volume filtration (circles) of the supra-POM samples. Shaded coloured areas show
494 the sampling area covered to harvest each supra-POM sample. Sea-ice extent and
495 concentration at the beginning (c), in the middle (d) and at the end (e) of the sampling
496 campaign. The ship position is shown by a filled red circle.



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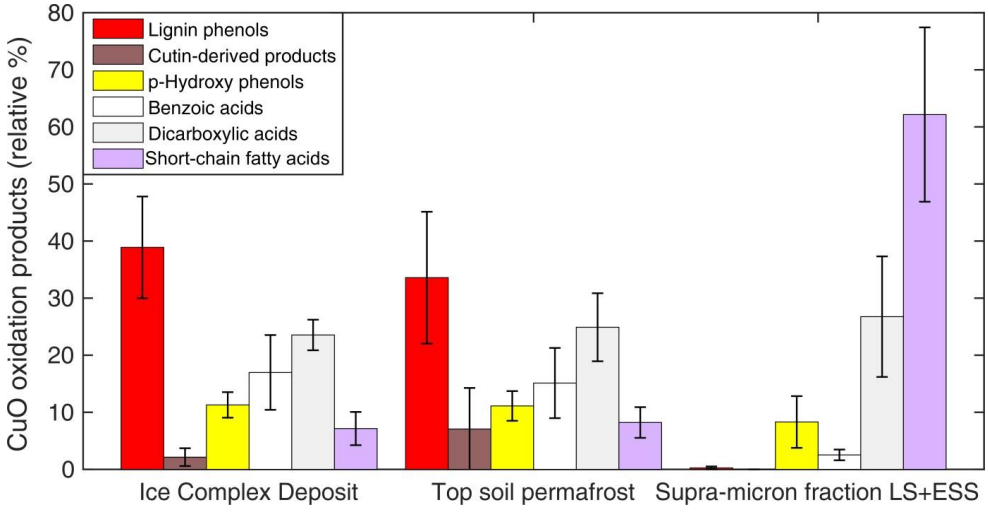
499 **Fig.2** Surface water properties. (a) Salinity. (b) DOC. (c) δ^{13}C-DOC. (d) CO_2aq. (e) δ^{13}C-
500 CO_2aq. Shaded areas show the sea-ice extent at the beginning (13/07/2014) and at the end of
501 the sampling campaign (14/08/2014) (Humborg et al., submitted; Salvadó et al., 2016; The
502 SWERUS-C3 Scientific Party, 2016).



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507 **Fig.3** Alkaline CuO fingerprint of top-soil permafrost samples (Tesi et al., 2014), Pleistocene
508 Ice Complex Deposit (Tesi et al., 2014) and supra-POM fraction (this study). The plot
509 displays the relative proportion of the CuO oxidation products.

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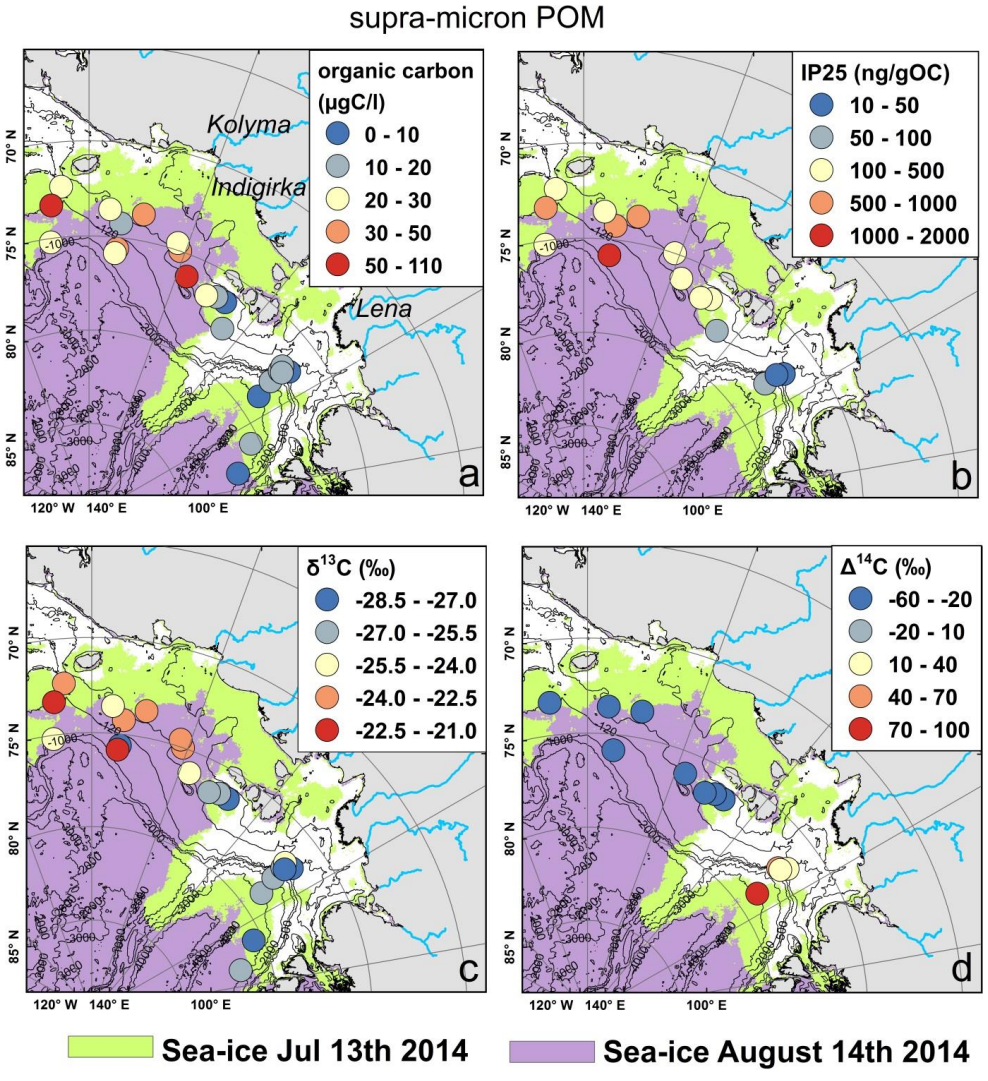

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522 **Fig. 4** Supra-POM composition. (a) Organic carbon concentration. (b) IP25 (mono-
523 unsaturated highly branched isoprenoid. (c) $\delta^{13}C$. (d) $\Delta^{14}C$. Shaded areas show the sea-ice
524 extent at the beginning (13/07/2014) and at the end of the sampling campaign (14/08/2014).
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530 **Fig. 5** SEM images. (a) ST-11: Dinoflagellates (*Protoperidinium* spp.) in open-waters of the
531 Laptev Sea. (b) ST22: Diatoms, mostly spines (setae) of *Chaetoceros* spp. in the transition
532 between Laptev Sea and East Siberian Sea. (c) ST-34: Diatoms from sea-ice dominated
533 waters in the East Siberian Sea

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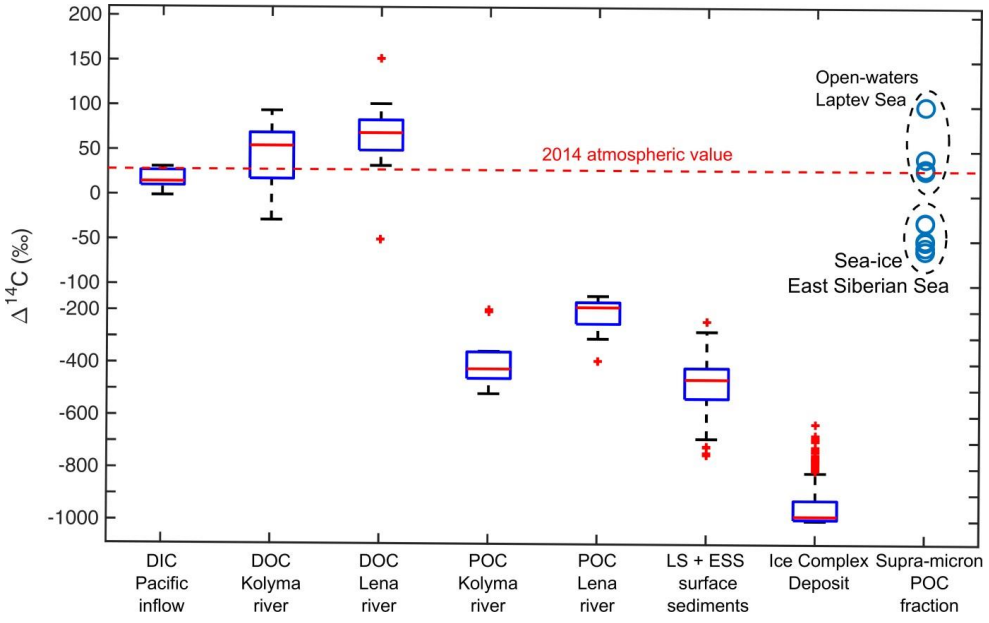

Fig. 6 Radiocarbon signature of inorganic and organic carbon pools. Whisker plots of radiocarbon values for different inorganic and organic carbon sources from the literature, compared to the outer Laptev Sea and outer East Siberian Sea (blue circles, this study). Solid lines show the median, the box limits display the 25th and 75th percentiles while the crosses show the outliers. Source: DIC (Griffith et al., 2012), DOC-Kolyma (2009-2014), DOC-Lena (2009-2014), POC-Kolyma (2009-2011), POC-Lena (2009-2011) (www.arcticgreatrivers.org), Laptev Sea and Eastern Siberia Sea surface sediments (Salvadó et al., 2016; Vonk et al., 2012) and Ice Complex Deposit (Vonk et al., 2012).

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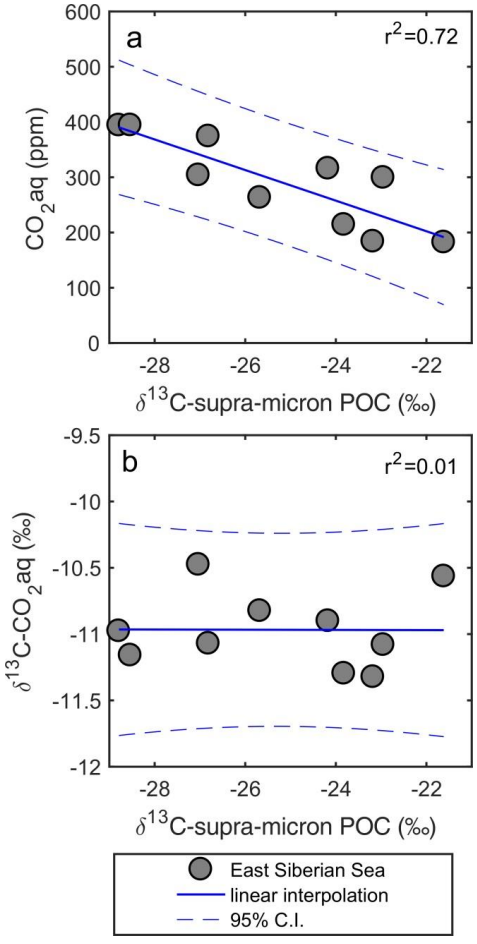

Fig. 7 Correlations (a) CO_2aq vs $\delta^{13}C$ (supra-micron POM fraction) and (b) $\delta^{13}C$-CO_2aq vs $\delta^{13}C$ in the East Siberian Sea (filled circles). The solid line shows the linear interpolation while the dashed line shows the 95% confidence intervals.

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