Ardiningsih, I.; Krisch, S.; Lodeiro, P.; Reichart, G.-J.; Achterberg, E.P.; Gledhill, M.; Middag, R. & Gerringa, L.J.A. (2020). Natural Fe-binding organic ligands in Fram Strait and over the northeast Greenland shelf. *Marine Chemistry*, 224, 103815

Published version: https://dx.doi.org/10.1016/j.marchem.2020.103815

NIOZ Repository: http://imis.nioz.nl/imis.php?module=ref&refid=328453

Research data: https://doi.org/10.25850/nioz/7b.b.u

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Natural Fe-binding organic ligands in Fram Strait and over the northeast Greenland shelf

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There is a paucity of data on Fe-binding ligands in the Arctic Ocean. Here we investigate the distribution and chemical properties of natural Fe-binding ligands in Fram Strait and over the northeast Greenland shelf, shedding light on their potential sources and transport. Our results indicate that the main sources of organic ligands to surface waters of Fram Strait included primary productivity and supply from the Arctic Ocean. We calculated the mean total Fe-binding ligand concentration, [L_t], in Polar Surface Water from the western Fram Strait to be 1.65±0.4 nM eq. Fe. This value is in between reported values for the Arctic and North Atlantic Oceans, confirming reports of north to south decreases in [L_t] from the Arctic Ocean. The differences between ligand sources in different biogeochemical provinces, resulted in distinctive ligand properties and distributions that are reflected in [L_t], binding strength (log $K'_{Fe'L}$) and competing strength (log $\alpha_{Fe'L}$) of ligands. Higher [L_t] was present near the Nioghalvfjerdsfjorden (79N) Glacier terminus and in the Westwind Trough (median of [L_t] = 2.17 nM eq. Fe; log $K'_{Fe'L}$ = 12.3; log $\alpha_{Fe'L}$ = 3.4) than in the Norske Trough (median of [L_t] = 1.89 nM eq. Fe; log $K'_{Fe'L}$= 12.8; log $\alpha_{Fe'L}$ = 3.8) and in Fram Strait (median of [L_t] = 1.38 nM eq. Fe; log $K'_{Fe'L}$ = 13; log $\alpha_{Fe'L}$= 3.9). However, organic ligands near the 79N Glacier terminus and in the Westwind Trough were weaker, and therefore less reactive than organic ligands in the Norske Trough and in Fram Strait. These weaker ligands, although more abundant than in the Fram Strait, reduce overall Fe solubility in waters transported from the 79N Glacier to Fram Strait. The lower ligand binding strength in the outflow results in a higher inorganic Fe concentration, [Fe´], which is more prone to precipitation and/or scavenging than Fe complexed with stronger ligands. Ongoing changes in the Arctic and sub-Arctic Oceans will influence both terrestrially derived and *in-situ* produced Fe-binding ligands, and therefore will have consequences for Fe solubility and availability to microbial populations and Fe cycling in Fram Strait.

Introduction

The Arctic region is undergoing rapid environmental changes (Gascard et al., 2008; IPCC, 2014), including permafrost (Schuur et al., 2015) and ice-sheet melt (Ekwurzel et al., 2001). The environmental alteration induced by climate changes will influence the biogeochemical cycle of many elements, including iron (Fe), an important micronutrient regulating the dynamics of primary productivity (Boyd et al., 2000; De Baar, 1990; Martin and Fitzwater, 1988; Rijkenberg et al., 2018). In the shelf-dominated Arctic Ocean, the Polar Surface Water (PSW) is strongly influenced by runoff from Eurasian rivers with waters reaching the central basin via the Transpolar Drift (TPD) (Gascard et al., 2008; Gordienko and Laktionov, 1969), and lateral transport over the shelf areas. The runoff introduces organic matter, fluvial sediment, and other terrigenous materials (Ekwurzel et al., 2001; Klunder et al., 2012; Measures, 1999). These materials contribute organic ligands of terrestrial origin, mainly humics (Laglera et al., 2019a; Slagter et al., 2019). The organic ligands stabilize Fe in the dissolved form, and prevent Fe from precipitating (Kuma et al., 1996; Millero et al., 2002), thereby enabling a substantial amount of dissolved-Fe (DFe) to be present in PSW (Klunder et al., 2012; Rijkenberg et al., 2018; Slagter et al., 2017). Determining the complexation of Fe with organic ligands is, thus, a crucial component of Fe biogeochemistry. The PSW, enriched in DFe bound to terrestrially derived organic ligands as well as ligands produced in the Arctic Ocean, can be transported out of the central Arctic via Fram Strait (Laukert et al., 2017; Slagter et al., 2019), a main gateway for heat and water mass exchange between the Arctic Ocean and the Nordic Seas (Greenland Sea, Norwegian Sea and Iceland Sea) (Rudels et al., 2005; Rudels et al., 2015). In the vicinity of Fram Strait, the Nioghalvfjerdsfjorden (79N) Glacier terminates on the northeast Greenland shelf, where the Norske Trough and Westwind Trough are located. The ongoing changes in the Arctic and sub-Arctic Oceans will influence the sources of Fe-binding organic ligands, and therefore have consequences for DFe supply and transport, particularly in Fram Strait. However, there is a paucity of data to comprehensively assess the effect of global climate change on the biogeochemical cycle of DFe as well as associated feedback mechanisms.

Iron is present at sub-nanomolar levels in oceanic water due to its low solubility and low supply rate (Liu and Millero, 2002), limiting primary productivity in approximately one third of the global ocean (Boyd et al., 2000; De Baar, 1990; Martin and Fitzwater, 1988; Rijkenberg et al., 2018). In seawater, DFe can exist in two different oxidation states, Fe(II) and Fe(III). The Fe(III) oxidation state dominates the chemical speciation of DFe around pH 8 in oxygenated waters, forming Fe oxy-hydroxides (Kuma et al., 1996). At the natural seawater pH, Fe oxy-

hydroxides tend to undergo further hydrolysis, and are thus prone to precipitation. However, organic complexation by Fe-binding ligands shifts the equilibrium reaction away from Fe hydrolysis (Kuma et al., 1996; Millero et al., 2002), governing Fe solubility in seawater (Gledhill and Buck, 2012; Hunter and Boyd, 2007). Despite its importance in determining Fe solubility, Fe-binding ligand data is scarce, notably in ice-covered Arctic and subarctic regions.

To date, only a few studies have looked at Fe-binding ligands in the subarctic and Arctic Ocean. Thuróczy et al. (2011) presented the first dataset on Fe fractionation and organic chelation in the central Arctic. Recently, the terrestrial influence on organic ligands in surface waters of the Arctic Ocean was investigated (Slagter et al., 2017). The high concentrations of DFe (up to 4.4 nM) in PSW (Klunder et al., 2012; Rijkenberg et al., 2018) were facilitated by complexation with enhanced concentrations of organic ligands (Slagter et al., 2017). This surface DFe enhancement was a clear indication of a riverine contribution in the flow path of the TPD in the Arctic Ocean. The DFe and Fe-binding ligand concentrations were up to 4.5 and 1.7 times higher inside than outside the flow of the TPD, respectively, and ligands from terrestrial origin dominated the total ligand pool in the TPD (Laglera et al., 2019a). This indicates a transport of organic Fe-binding ligands via the TPD (Slagter et al., 2019), and these ligands are likely transported out of the Arctic Ocean towards Fram Strait.

The concentrations and conditional stability constants (K'_{FeL}) of Fe-binding ligands in seawater are typically determined by the electrochemical technique known as competitive ligand equilibration (CLE) – adsorptive cathodic stripping voltammetry (AdCSV). This technique is based on the competitive equilibrium between an added known ligand and natural ligands present in seawater (Abualhaija and van den Berg, 2014; Croot and Johansson, 2000; Gledhill and van den Berg, 1994; Rue and Bruland, 1995; van den Berg, 2006). A distribution of conditional stability constants is commonly used to classify Fe-binding ligand groups (Gledhill and Buck, 2012), although the boundaries between the groups are still indistinct and probably more gradual than first assumed. In short, three key groups are acknowledged, (i) strong Fe-binding siderophores (Mawji et al., 2008; Velasquez et al., 2016; Vraspir and Butler, 2009), (ii) relatively weak Fe-binding humic substances (Bundy et al., 2014; Laglera and van den Berg, 2009), and (iii) relatively weak Fe-binding microbially-excreted sugars such as polysaccharides or exopolymeric substances (Hassler et al., 2011). Siderophores are defined as low-molecular-weight organic compounds (<1kDa) secreted by prokaryotes as part of an Fe-uptake system (Mawji et al., 2008; Vraspir and Butler, 2009). Humic substances (HS) typically come from the degradation of organic matter; they have a strong terrestrial component in the Arctic and are

substantially resistant to degradation (Calace et al., 2001; Laglera et al., 2019a; Laglera and van den Berg, 2009). However, marine HS can also be produced *in situ* by bacterial remineralization of biogenic particles (Burkhardt et al., 2014) and grazing (Decho and Gutierrez, 2017; Laglera et al., 2019b). Exopolymeric substances (EPS) are relatively labile macromolecules excreted by microbial cells during all life cycles of phytoplankton growth (Decho and Gutierrez, 2017). During an extreme bloom and following its termination, EPS can dominate from 1% to 50% of the dissolved organic carbon (DOC) pool (Orellana et al., 2003) and together with HS, can be a significant contributor of colloidal organic ligands (Batchelli et al., 2010; Hassler et al., 2011). As microbial exudates, EPS are expected to be produced abundantly up to micromolar levels in surface waters, also at the base of sea ice (Lannuzel et al., 2015), showing the potential to outcompete the stronger ligand group (Hassler et al., 2011). The classification of weak and strong ligand groups based on these three groups is challenging. For example, Slagter et al. (2019) concluded that HS, thought to be a weaker ligand group, can also contain relatively strong ligands (log K'_{FeL} 11.5 – 12.6), whereas Norman et al. (2015) demonstrated that EPS could have strong binding stability constants as well (log K'_{FeL} >12).

This study focuses on the distribution and chemical properties of natural Fe-binding ligands in Fram Strait and over the northeast Greenland shelf. Concentrations of dissolved and total dissolvable Fe of the same expedition (Krisch et al., submitted) are here combined with the distribution and chemical properties of natural Fe-binding ligands in Fram Strait and over the northeast Greenland shelf (77°N – 81°N and 20°W – 20°E), shedding light on their potential sources and transport and further elucidate the cycling of both Fe and Fe-binding ligands in the rapidly changing Fram Strait region.

Material and methods

Sampling

Samples were obtained during GEOTRACES expedition GN05 (PS100) on the German research vessel Polarstern during summer 2016. Seawater samples for trace metals and ligands were sampled between 22nd July and 1st September. Details about the cruise track, ice-cover and hydrographic data can be found in the expedition report (Kanzow, 2017).

A total of 10 stations were sampled as full depth profiles, 8 - 12 ligand samples per station in Fram Strait and 5 - 7 samples per station over the shelf. Conductivity, temperature, depth (CTD), oxygen and turbidity profiles were obtained using a titanium Seabird SBE 911plus on a trace metal clean rosette frame. The frame was equipped with 24 x 12 L Go-Flo bottles (Ocean

Test Equipment) and seawater was collected following the sampling procedures as described by Cutter (2010). Across Fram Strait, samples were collected from 4 different stations (1, 7, 14 and 26). Station 1 was located on the eastern side of Fram Strait close to the Svalbard archipelago, while stations 7, 14 and 26 were located towards the western side of Fram Strait (Figure 1). The northeast Greenland shelf section consisted of 6 stations covering the Norske-Westwind trough system, 3 stations were sampled in the Norske Trough (17, 18, and 19) and 1 station (11) was sampled in the Westwind Trough (Figure 1). In addition, 2 more stations (21 and 22) were sampled in front of the largest glacier of northeast Greenland, the 79N Glacier (Schaffer et al., 2017). Station 21 was located ~20 km away from the glacier front, and station 22 was located in front of the floating glacier ice-tongue.

Immediately after recovery of the CTD rosette, the Go-Flo bottles were carried into a trace metal clean sampling-container where sub-sampling and filtration was performed under N_2 overpressure (~0.2 Bar) using 0.2 µm filters (Acropack 0.8/0.2 µm cartridge filter, Pall). The samples for dissolved Fe analysis were collected in low density polyethylene bottles (LDPE, 125 mL~~l~~, Nalgene) immediately acidified to pH 1.8 using ultraclean HCl (Romil Suprapure) on board as described elsewhere (Krisch et al., submitted).

Samples for Fe-binding ligand analysis were collected into acid-cleaned 1000 mL LDPE bottles, immediately stored at -20°C after sampling, and transported to the NIOZ laboratory for analysis. Prior to analysis, samples were thawed in the dark and sub-samples were taken to determine DFe present in the ligand sample bottles for calculation of total Fe-binding ligand concentrations. Therefore approximately 50 mL was collected into 60 mL pre-cleaned LDPE bottles and acidified to pH ~1.8 using concentrated ultrapure hydrochloric acid into final concentration ~0.024 µM (0.2% v/v; Seastar chemicals). The acidified samples were stored at room temperature prior to analysis.

Material handling

Before use, sample bottles were cleaned following three-step cleaning procedure for trace element sample bottles (Cutter, 2010; Middag et al., 2009). All chemicals were prepared using ultrapure water (18.2 MΩ cm, Milli-Q element system, Merck Millipore) and handling performed in an ISO class 7 ultra-clean laboratory with ISO class 5 workspaces. Outside the ultraclean environment, samples were handled in a laminar flood hood (ISO class 5, interflow and AirClean systems).

Iron analysis

Analysis of DFe was done twice, at GEOMAR, Kiel (Krisch et al., submitted) in samples acidified immediately shipboard, and in subsamples taken from the ligand samples at NIOZ, Texel. In the laboratory at GEOMAR, DFe concentrations were measured by isotope dilution high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS, Thermo Fisher Element XR) after pre-concentration (Rapp et al., 2017). The detailed procedure for DFe determination described elsewhere (Krisch et al., submitted).

For calculation of [L_t] values, we used the DFe measured from the same bottles as the ligand samples. The DFe samples were pre-concentrated using an automated SeaFAST system (SC-4 DX SeaFAST pico; ESI), and analyzed by HR-ICP-MS (Thermo Fisher Element XR) with quantification via standard additions. Accuracy and reproducibility were checked by regular measurements of reference material SAFe D1 (#169) and in-house standards. Results for DFe analyses of reference materials were within the range of May 2013 consensus values (SI Table 1). The average overall method blank (SeaFAST & ICP-MS) concentration, determined by measuring acidified ultrapure water as a sample, was 55±7 pM. Dissolved-Fe concentrations measured from the ligand bottles were approximately 15% (n = 69) lower than DFe measured from immediately acidified samples as also found by Gerringa et al. (2014)

Fe-binding ligands analysis (TAC Method)

The CLE-AdCSV technique using 2-(2-thiazolylazo)-p-cresol (TAC, Alfa Aesar) was employed to determine the total Fe-binding ligand concentrations, [L_t] and K'_{FeL} (Croot and Johansson, 2000).

A Hanging Mercury Drop Electrode stand (VA663 Metrohm), connected to a PC via an interface (IME663) to control the potentiostat (μAutolab III, Metrohm Autolab B.V.) was used. The electrodes in the voltammetric stand included a standard Hg drop working electrode, a glassy carbon counter electrode and a double-junction Ag/AgCl reference electrode (3M KCl). For the titration, 10 mL subsample aliquots were distributed into the pre-conditioned Teflon (30 mL Savillex) vials, and buffered to a final pH of 8.05 with MnO_2-cleaned borate-ammonium (Merck) buffer (final concentration 5 mM). An Fe standard working solution was added to the sample vials, resulting into final concentrations of 0 (twice, no Fe addition); 0.2; 0.4; 0.6; 0.8; 1; 1.2; 1.5; 2; 2.5; 3; 4; 6; 8 (twice) nM of Fe. The purpose of double measurement of the no Fe additions was to be absolutely sure this measurement was not influenced by an unconditioned

cell. Based on our experience, a small error of the measurement of the highest addition of the titration has large an effect on the result. Therefore, these points were done twice and the ones that gave the best fit were used for the calculation. After Fe additions, TAC was added to each vial at a final concentration of 10 µM. The content in the vials was allowed to equilibrate for at least 8 hours before analysis or typically overnight (Croot and Johansson, 2000). For analysis, the voltammetric scans were in the differential-pulse mode, with a modification from the original procedure (Croot and Johansson, 2000) as previously reported by Slagter et al. (2017). For each sample, two duplicate scans were done at a deposition time of 140s.

Fe speciation calculations

The data obtained by CLE-AdCSV was interpreted for the ligand parameters, $[L_t]$ and $K'_{Fe'L}$. The data were fitted by a Langmuir model using non-linear regression using the software package R (R Development Core Team, 2011) as described by (Gerringa et al., 2014). A one-ligand model was applied, assuming a single ligand group existed. This model fitted the data well (SD < 2%; SD of the fitted data from the Langmuir model). The total Fe-binding ligand concentration, $[L_t]$, is reported in nM equivalents of Fe (nM eq. Fe) and $K'_{Fe'L}$ values are reported as a common logarithm to base 10 value ($\log K'_{Fe'L}$) with respect to inorganic Fe (Fe′). The prime symbol (′) is used to denote the fraction not bound by L. For the purpose of this paper, we define $\log K'_{Fe'L}$ as the binding strength of ligands.

The values of $[L_t]$ and $\log K'_{Fe'L}$ were combined with DFe, measured at GEOMAR to derive concentrations of inorganic Fe, [Fe′]. The Fe′ species are predominantly Fe-hydroxides, and at a fixed pH of 8.05, [Fe′] can be calculated (Hudson et al., 1992; Liu and Millero, 2002). The calculation of the ligand parameters is described elsewhere (Gerringa et al., 2014; Ružić, 1982; van den Berg, 1982).

The center of detection window (D) determines which ligand groups, with respect to their conditional binding strength, can be determined. D is defined as the product of the concentration of TAC and the conditional stability constant of $Fe(TAC)_2$, $\beta'_{Fe'(TAC)2}$.

$$D_{TAC} = [TAC]^2 \times \beta'_{Fe'(TAC)2}$$

The inorganic side reaction coefficient of Fe ($\alpha_{Fe'}$) of $10^{10.31}$, as determined using Visual MINTEQ software (Gustafsson, 2011), was used to transform the $\beta'_{Fe'(TAC)2}$ after Croot and Johansson (2000) with respect to Fe^{3+}, into the one with respect to Fe′. Hence, $\beta'_{Fe'(TAC)2} = 10^{12.1}$

was used, resulting in log D_{TAC} = 2.1. The range of the detection window is assumed to be one order above and below log D_{TAC} (Apte et al., 1988).

The side reaction coefficient $\alpha_{Fe'L}$ reflects the ability of ligands to compete for Fe with other ligands and particles. We define $\alpha_{Fe'L}$ here as the competing strength of ligands, expressed as a logarithmic value, log $\alpha_{Fe'L}$. The saturation state of ligands is indicated by the ratio of $[L_t]/[DFe]$. Assuming that other competing metals can be neglected, ligands are undersaturated when $[L_t]/[DFe] > 1$, whereas $[L_t]/[DFe] \leq 1$ indicate that the ligands are close to saturation (Thuróczy et al., 2010). Statistical analysis of a t-test was performed using the software package R.

Results

Hydrography

The hydrographic features of Fram Strait have been described in detail elsewhere (Beszczynska-Möller et al., 2012; Laukert et al., 2017; Richter et al., 2018; Rudels et al., 2005; Swift and Aagaard, 1981) and are summarized briefly in this study. Water masses were identified using conservative temperature (Θ in ^{o}C) and absolute salinity (S_A in g/kg) plots following definitions by Tomczak and Godfrey (2003). The data of Θ and S_A were derived from the CTD data using Ocean Data View (Schlitzer, 2018).

The relatively warm Atlantic Water (AW) flows northward, carried by the West Spitsbergen Current (WSC) at depths shallower than ~500 m at station 1 (Figure 2a). In Fram Strait, about half of AW recirculates back southward, and the other half continues northward into the Arctic Ocean, where it is cooled and freshened, forming Arctic Atlantic Water (AAW) in the process (Bourke et al., 1987; Laukert et al., 2017). The AAW is modified by Pacific-origin water and a large amount of terrestrial runoff in the central Arctic before exiting back through Fram Strait. This modified AAW flows out of the Arctic Ocean along with PSW. These water masses flow southward carried by the East Greenland Current (EGC) (Laukert et al., 2017; Richter et al., 2018; Rudels et al., 2005) in western Fram Strait (at stations 14 and 26; Figure 2a). The western and middle Fram Strait section is substantially affected by the southward flowing Recirculating-Atlantic Water (RAW). The mixing product of RAW (~200 to ~500 m) and PSW (upper ~300 m), known as warmer PSW (PSWw) (Rudels et al., 2005; Swift and Aagaard, 1981), was observed in surface waters in between the EGC and WSC at station 7 (Figure 2a). On both sides of Fram Strait, Atlantic Intermediate Water (AIW) (Bourke et al., 1987; Rudels et al., 2005) was present at ~500 to ~900 m depth, and Norwegian Sea Deep Water (NSDW) (Laukert et al., 2017; Swift and Aagaard, 1981) was present below 1000 m. In this study, AIW and NSDW are categorized as deep waters.

Along the northeast Greenland shelf transect, the bathymetry is characterized by the Norske-Westwind Trough system (Figure 1), that features a deep sill in the Norske Trough and a shallow sill in the Westwind Trough (Schaffer et al., 2017). Along this transect, the surface circulation in the C-shaped trough system carried PSW into the Norske-Westwind Trough system in the upper 150-200 m (Bourke et al., 1987; Schaffer et al., 2017). Underneath the PSW layer, modified-AIW (mAIW) was found deeper than ~200-250 m (Figure 2b). For the purpose

of this study, mAIW is differentiated as warm-mAIW in the Norske Trough and cold-mAIW in the Westwind Trough based on Schaffer et al. (2017).

Dissolved-Fe and Fe-binding ligands

Here we present DFe profiles (Figures 3a and 3b) from stations for which Fe-binding ligand samples were also taken. Higher resolution DFe profiles from GEOTRACES expedition GN05 are reported by Krisch et al. (submitted).

The Fram Strait transect

DFe concentrations in Fram Strait were in the range of 0.28-1.64 nM. Concentrations of DFe in Fram Strait were low in surface waters (median AW = 0.59 nM, PSWw = 0.76 nM, PSW = 0.48 nM) and increased towards the seafloor to 1.28 nM. On the eastern side, a maximum in DFe was present at ~500 m (1.64 nM). This elevated DFe decreased horizontally westward from station 1 in the east to stations 14 and 26 in the west to concentrations of 0.37 nM (Figure 3a).

In Fram Strait, [L_t] ranged from 0.79 to 3.00 nM eq. Fe (median AW = 1.20 nM eq. Fe, PSWw = 1.77 nM eq. Fe, PSW = 1.78 nM eq. Fe, deep waters=1.36 nM eq. Fe; SI Table 2). At stations on the western side (14 and 26), [L_t] was generally higher than at stations in the east and central Fram Strait (1 and 7; Figure 3b). The ratio [L_t]/[DFe] varied between 0.5 and 5.4 (Figure 4a). In the central and eastern regions (stations 1 and 7), the ratio decreased below 250 m, whereas it remained high on the western side of Fram Strait (stations 14 and 26). The ligands were saturated with Fe ([L_t]/[DFe] < 1) at 500 m depth at station 1 and nearly saturated near the sea floor.

Whilst [L_t] in surface waters of Fram Strait generally increased from AW (median=1.20 nM eq. Fe) in the east to PSW (median=1.77 nM eq. Fe) in the west (Figures 3b and 5a), the median of [Fe´] in Fram Strait was relatively uniform at 0.05 – 0.15 pM (Figure 5b), apart from the two samples where organic ligands were saturated with Fe.

A considerable variation was observed in log $K'_{Fe'L}$ values (Figure 6a) that ranged from 11.8 to 13.9 (median AW = 13.3, PSWw = 12.9, PSW = 12.4, deep waters = 13.0; Figure 6a). The values of log $\alpha_{Fe'L}$ (Figure 6b) varied between 1.3 and 4.7 (median AW=4.0, PSWw=3.7, PSW=3.4, deep waters=3.9; Figure 6b). The highest log $\alpha_{Fe'L}$ value falls more than 2 orders of magnitude above the log D_{TAC} and thus the highest log $K'_{Fe'L}$ could not be estimated accurately.

Since the ligands were saturated with DFe at 500 m depth at station 1, the calculated α_{FeL} does not represent the actual value of ligand competing strength and thus this data point was not used for calculations.

The northeast Greenland shelf transect

Concentrations of DFe ranged from 0.58 to 1.45 nM in PSW (median DFe = 0.92 nM) and 0.55 to 0.78 nM in warm-mAIW (median DFe = 0.68 nM) in the Norske Trough (Figure 3c). Near the 79N Glacier terminus and Westwind Trough, DFe concentrations ranged from 0.71 to 2.10 nM (median DFe = 1.16 nM) in PSW and 0.63 to 1.38 nM in cold-mAIW (median DFe = 0.77 nM). The highest DFe concentration (2.10 nM) was found in PSW at 30 m depth in front of the glacier terminus (station 22).

In the Norske Trough, [L_t] varied from 1.41 to 3.60 nM eq. Fe in PSW and 0.97 to 2.26 nM eq. Fe in warm-mAIW, whereas near the glacier terminus and Westwind Trough, [L_t] ranged from 1.88 to 2.64 nM eq. Fe in PSW and 2.08 to 2.38 in cold-mAIW (Figure 3d, SI Table 2). On average, [L_t] was slightly higher at stations near the glacier terminus (stations 21 and 22) than in the Norske Trough, although the highest [Lt] existed in PSW in the Norske Through (station 18) with values up to 3.60 nM eq. Fe at 30 m depth. The ratio of [L_t]/[DFe] ranged between 1 and 4.4 (Figure 4b), indicating that Fe-binding ligands along the northeast Greenland shelf transect were undersaturated. Near the seafloor at station 19 (Norske Through) and at 50 m depth at station 22 (glacier terminus), nearly saturated ligands were observed.

Generally, organic ligands were present at higher concentrations in PSW and mAIW near the glacier terminus and Westwind Trough than in the Norske Trough and Fram Strait (Figure 5a). High concentrations of [Fe´] were found in PSW and cold-mAIW in front of the floating glacier ice-tongue (Figure 5b), where the organic ligands were nearly saturated (at station 22; Figure 4b). Excluding high [Fe´] concentrations in samples where organic ligands were nearly saturated, the median of [Fe´] in PSW and mAIW was lower in the Norske Trough (0.16 and 0.13 pM) than the Westwind Trough and near the glacier terminus (0.41 and 0.33 pM) (Figure 5b).

The log K'_{FeL} ranged from 12.4–13.2 in the Norske Trough (median PSW=12.7, warm-mAIW=12.9; Figure 6a). Near the glacier terminus and in the Westwind Trough, the log K'_{FeL} ranged from 12.0 – 12.9 (median PSW and cold-mAIW=12.3, warm-mAIW=12.9; Figure 6a). The log K'_{FeL} in the northeast Greenland shelf waters were on average lower than in Fram Strait

(Figure 6a). The median values of log $\alpha_{Fe'L}$ in PSW and warm-mAIW in the Norske Trough were 3.9 and 3.7, respectively. In the Westwind Trough and in front of glacier terminus, the median values of log $\alpha_{Fe'L}$ were 3.5 in PSW and 3.4 in cold-mAIW. In general, variation in log $\alpha_{Fe'L}$ values over the northeast Greenland shelf was less than in Fram Strait (Figure 6b).

Discussion

The applied method using TAC was reported to underestimate [L_t] due to an interaction of TAC with HS binding sites (Laglera et al., 2011; Slagter et al., 2019). However, this method did reveal HS involvement in the ligand pool in different environments (Batchelli et al., 2010; Dulaquais et al., 2018), even in the TPD flow path, where the HS ligands were the dominant group (Slagter et al., 2017). Slagter et al. (2019) compared two CLE-AdCSV techniques, TAC and salicylaldoxime (SA) in the Arctic Ocean and concluded that an offset in [L_t] between the methods existed. Yet, the increase in [L_t] due to HS ligands in the TPD was the same for both methods. Thus in our study, we assume that HS is detectable by the TAC method, although [L_t] might be underestimated.

Comparison to previous studies

Natural ligand measurements have not previously been reported for Fram Strait, but data is available for adjacent areas, notably the Northern Atlantic (Buck et al., 2015; Gerringa et al., 2015; Mohamed et al., 2011) and Arctic Ocean (Slagter et al., 2017; Thuróczy et al., 2011). The studies conducted by Thuróczy et al. (2011), Gerringa et al. (2015) and Slagter et al. (2017) used the same analytical method and data processing technique as in this study, allowing a direct comparison. The here reported [L_t] in Fram Strait (median PSW = 1.78 nM eq. Fe, PSWw = 1.77 nM eq. Fe, SI Table 2) is comparable to the median [L_t] (1.61 nM eq. Fe) outside the TPD flow path (Slagter et al., 2017), but slightly higher than [L_t] reported by Gerringa et al. (2015) for the region between 60 and 33°N in the north west Atlantic Ocean where the median [L_t] was 1.2 nM eq. Fe (N=8) and reached up to 3.3 nM eq. Fe (SI Figure 2). The median [L_t] in PSW in the western Fram Strait (1.78 nM eq. Fe) and in the northeast Greenland shelf waters (1.96 and 2.17 nM eq. Fe, SI Table 2; surface shelf waters = 2.06 nM eq. Fe; SI Figure 2) was comparable to the median [L_t] (2.02 nM eq. Fe) reported by Thuróczy et al. (2011) for the Arctic Ocean, but lower than the average [L_t] (2.79±0.92, N=19) inside the TPD flow path (Slagter et al., 2017). The elevated [L_t] in the TPD has been related to HS ligands from fluvial input as well as interaction between sea-ice and sediment (Slagter et al., 2017 and references therein). Gerringa et al. (2015) hypothesized that the Arctic is a source of ligands, largely of humic

origin, to the North Atlantic and that [L_t] decreases over time and distance during advection to the south with North Atlantic Deep Water. The current data in Fram Strait indeed confirmed the Arctic can be a source of ligands, likely of humic origin, to regions to the south.

We found high [L_t] up to 3.6 nM eq. Fe in the sea-ice covered PSW in the Norske Trough (station 18). Antarctic sea ice is known to be a source of ligands, probably due to EPS excretion at the bottom of the sea ice by diatoms. According to Lannuzel et al. (2015), abundant sea ice diatoms were responsible for relatively high [L_t] in under-ice seawater (4.9 to 9.6 nM eq. Fe; log K'_{FeL} ~11 to 13 measured with 1-nitroso-2-napthol), indicating that EPS could increase [L_t] in seawater with sea-ice coverage. As far as we know, no ligand data of Arctic sea ice is available, but the high [L_t] in the sea-ice covered in the Norske Trough, was only slightly lower than the [L_t] reported by Lannuzel et al. (2015) and had comparable relatively high log K'_{FeL} (12.4 - 12.8). As detailed in the introduction, EPS were considered to be part of the weak ligand group (Buck et al., 2016; Bundy et al., 2014; Hassler et al., 2011; Hassler et al., 2017; Laglera and van den Berg, 2009), but Norman et al. (2015) demonstrated that EPS could have strong conditional stability constants (log K'_{FeL} >12), hence could contribute to the strong ligands detected in surface waters, especially in regions with sea-ice coverage (Krembs et al., 2002; Lannuzel et al., 2015; Lin and Twining, 2012). Thus we suggest that the high [L_t] in sea-ice covered Norske Trough is possibly due to EPS.

Organic ligand sources in Fram Strait

A considerable variation in log K'_{FeL} values (median AW = 13.3, PSWw = 12.9, PSW = 12.4; Figure 6a), suggests varying contributions of relatively strong and weak ligand groups to the overall ligand pool. The Fe-binding ligands in surface waters of Fram Strait were dominated by a strong ligand group as apparent from the relatively high log K'_{FeL}(>12; Figure 6a). Despite seasonal NO_3 depletion (Hopwood et al., 2018), this area is productive (Cherkasheva et al., 2014; Smith Jr. et al., 1987). Primary productivity is a known source of organic ligands in surface waters as high ligand concentrations are often associated with high chlorophyll-*a* concentrations (Boye et al., 2001; Gledhill and Buck, 2012; Hunter and Boyd, 2007; Rue and Bruland, 1995; van den Berg, 1995). Besides releasing EPS, marine bacteria (*Alteromonas sp*.) can also synthesize siderophores during a bloom (Hogle et al., 2016). Additionally, following the decline of a phytoplankton bloom, excessive production of EPS can occur (Decho and Gutierrez, 2017). A high weekly average of chlorophyll-*a* concentrations was observed using the MODIS satellite (https://giovanni.gsfc.nasa.gov/giovanni/), which indicates the presence of a phytoplankton bloom in June and July. Our sampling time in Fram Strait (end of July to early

August, 2016) coincided with the post-bloom period and therefore it seems likely that bloom-associated ligands are responsible for the relatively high concentration of strong ligands in surface waters of Fram Strait.

The surface ligand concentration (Figure 5a) on the western side of Fram strait (median PSW=1.78 nM eq. Fe) as well as further into central Fram Strait (median PSWw = 1.77 nM eq. Fe) was somewhat higher than in eastern Fram Strait (median AW = 1.20 nM eq. Fe). Lateral transport of TPD-carried HS ligands from the Arctic (Laglera et al., 2019a; Slagter et al., 2019), likely formed an additional ligand source to surface waters of the western Fram Strait, where PSW flows south with the EGC in the upper ~150 m (Laukert et al., 2017; Richter et al., 2018). This implies both the phytoplankton bloom and TPD may play a role in the surface composition and distribution of ligands in Fram Strait. Atmospheric input does not seem to influence ligand concentrations, Rijkenberg et al. (2008) and Wagener et al. (2008) have shown that there is no input of aeolian Fe-binding ligands during dust deposition events, but dissolution of Fe from the dust does depend on the Fe-binding ligands present in seawater.

The organic ligands in Fram Strait were almost saturated near the seafloor (Figure 4a), notably in the region with elevated DFe concentrations (station 7). The western Fram Strait (stations 14 and 26) had relatively high, but variably distributed [L_t] over the water column (Figure 3b, SI Figure 1). Slope sediments can serve as a source of ligands to the deeper part of the water column (Buck and Bruland, 2007), however this does not seem to be the case for the station nearest to the slope (station 26), in contrast to the station further into Fram Strait (station 14). Possibly the water transport along the shelf break and interaction with the slope is not constant with time and place. Eddies exist at the shelf break and can reach deep enough to propagate subsurface waters (i.e AIW) toward the inner shelf (Schaffer et al., 2017; Topp and Johnson, 1997). In addition, here at this latitude (79^{o}N) the core of the southward flowing RAW mixes with the PSW, and thus substantially contribute to the EGC (Richter et al., 2018). Water transport driven by eddies and RAW intrusion to the EGC may explain the variably distributed [L_t] in the upper (~500m) water column, however, the elevated concentrations in the deeper part of station 14 remain unexplained.

Organic ligand sources over the northeast Greenland shelf

In this section, the transect over the northeast Greenland shelf will be discussed in the direction of the general circulation, starting at the southern inlet and going along the Norske Trough towards the 79N Glacier and back towards Fram Strait via the Westwind Trough. The water

masses from Fram Strait are propagated toward the inner shelf at the southern inlet (station 17), potentially by eddies, while undergoing pronounced mixing at the shelf edge. Eddy stirring and tidal mixing seem to be persistent features in the Norske Trough inlet (Bourke et al., 1987; Budéus et al., 1997; Schaffer et al., 2017). The balance between release and removal of organic ligands, along with physical water mass mixing (Budéus et al., 1997), is likely responsible for the fairly constant [L_t] observed in the water column at station 17 (Figure 3d).

The relatively high concentrations of strong organic ligands (up to 3.60 nM eq. Fe, log $K'_{Fe'L}$ 12.4-12.8) observed in PSW in the Norske Trough were most likely related to an earlier bloom, generating marine HS and EPS ligand groups with relatively strong affinity for Fe. The macro-nutrients (NO_3, PO_4, Si; data not shown) at this location were depleted and DFe was low (Figure 3d), indicative of a prior bloom. Consistently the chlorophyll-*a* concentration was low at the time of sampling (unpublished data), whereas higher concentrations were observed via satellite in the period prior to sampling (https://giovanni.gsfc.nasa.gov/giovanni/). Sato et al. (2007) showed a relation between increasing [L_t] and decreasing chlorophyll-*a* due to zooplankton grazing, and Laglera et al. (2019b) measured an increase in strong organic ligands as a consequence of grazing. This demonstrated that declining blooms can indeed contribute strong organic ligands and increase [L_t] as we observed in our study region. Additionally, black sea-ice with entrapped sediment was spotted during sampling at this location and the melting of black sea-ice can release HS ligands (Genovese et al., 2018) in addition to ligands released from grazing (Decho and Gutierrez, 2017; Laglera et al., 2019b). Also, we cannot eliminate the possible contribution of EPS, either produced *in situ* by sea-ice diatoms (Lannuzel et al., 2015) or released by phytoplankton cells after bloom termination (Decho and Gutierrez, 2017). Recent studies pointed out that HS and EPS can have strong Fe-binding sites (Laglera et al., 2019b; Lannuzel et al., 2015; Norman et al., 2015; Slagter et al., 2019). Therefore, the presence of HS and EPS can contribute to the pool of relatively strong ligands with elevated [L_t] in PSW in the Norske Trough.

The ligand-rich PSW in the Norske Trough did not seem to be a significant contributor of organic ligands to either the glacier front or the glacier outflow. Probably ligands produced in the Norske Trough did not yet reach the glacier front. In addition, newly produced ligands associated with primary productivity over the shelf, such as at station 18, are likely to be partially lost due to photodegradation (Barbeau et al., 2001; Powell and Wilson-Finelli, 2003), aggregation and sinking (Cullen et al., 2006) during transport. Either way, a high ligand concentration, such as in the surface waters of Norske Trough, was not observed at the glacier

terminus (at stations 21 and 22). At the 79N Glacier terminus, the 80-120 m thick ice-front is limiting direct entry of PSW into the glacier cavity, and at depths of ~80-270 m, water flows eastward away from the glacier front and into the trough system (Schaffer et al., 2017). As warm-mAIW in the Norske Trough has a relatively low [L_t], notably at station 19 on the northern end of the Norske Trough, ligands in the glacier outflow are thus likely produced in the glacier cavity itself. In general, meltwater is relatively poor in DOC compared to coastal seawater, but this DOC may be highly available to bacteria (Paulsen et al., 2017). Hence, the relatively high [L_t] over the entire water column near the 79N Glacier terminus (Figure 3d), could be associated with bacterial remineralization or byproducts of organic matter degradation (Gledhill and Buck, 2012; Gordienko and Laktionov, 1969; Hunter and Boyd, 2007). These ligands would be transported into the Westwind Trough, following the anti-cyclonic water circulation of the Norske-Westwind Trough system (Schaffer et al., 2017; Topp and Johnson, 1997). The median of log $K'_{\mathrm{Fe'L}}$, both in the PSW and mAIW near the glacier terminus (stations 21 and 22) and Westwind Trough (station 11) were somewhat lower (Figure 6a) than in the Norske Trough (median log $K'_{\mathrm{Fe'L}}$ =12.3 versus 12.7 and 12.9). This indicates that different ligand sources shift the characteristics of the overall ligand pool or the ligand pool has undergone physical, chemical or biologically-induced structural alterations during transport, e.g. through photo- or microbial degradation. Although ligands were present at higher concentrations (Figures 3d and 5a), these organic ligands were weaker than in the Norske Trough (Figure 6a). Primary productivity likely dominated the organic ligand sources in the Norske Trough, which may have led to a ligand pool with a relatively high conditional stability constant. In contrast, near the glacier terminus and in Westwind Trough, bacterial remineralization most likely was the dominant ligand source, resulting in more, but overall weaker ligands.

Near the glacier terminus and in Westwind Trough, [Fe´] was relatively high compared to Norske Trough and Fram Strait (Figure 5b). The glacier acts as a source of Fe and organic-ligand bound Fe, thereby facilitating glacial-Fe transport. However, at the glacier terminus, Fe was prone to precipitation and/or scavenging as [Fe´] was enhanced (Figure 5b) and the competing strength of the ligands (log $\alpha_{\mathrm{Fe'L}}$) was relatively low (Figure 6b). It should be noted here that the complexation of Fe by organic ligands is an equilibrium reaction between complexed Fe and [Fe´], where [Fe´] is not only determined by competing strength, but also by the scavenging intensity and precipitation reactions. Thus the ligands can effectively release Fe if their competing strength is relatively low and they are outcompeted by scavenging and

precipitation processes as shown in the deep Makarov Basin (Slagter et al., 2017; Thuróczy et al., 2011). Availability of [L_t] is thus not a guarantee for complexing (additional) DFe, as it is the overall equilibration between excess ligands, scavenging sites and precipitation that governs the fate of DFe.

Biogeochemical provinces of organic ligands

This study distinguished three biogeochemical provinces with respect to Fe-binding ligands, based on the influence of different sources of ligands, and hence ligand properties and distribution. The biogeochemical provinces include (1) Fram Strait, (2) Norske Trough and (3) near the glacier terminus and Westwind Trough. The different ligand properties and distribution are reflected in the differences in [L_t] (Figure 5a), log $K'_{Fe'L}$ (Figure 6a) and log $\alpha_{Fe'L}$ (Figure 6b).

As described above, in the northward flowing AW of the eastern Fram Strait, strong organic ligands derived from phytoplankton blooms are suggested to dominate the ligand pool. Whereas in the western Fram Strait in southward flowing PSW, part of the ligands probably originated from the Arctic Ocean and partly consists of HS ligands carried by the TPD (Slagter et al., 2017). The average log $K'_{Fe'L}$ is significantly higher (SI Table 3) in the AW flow (mean log $K'_{Fe'L}$ = 13.3±0.3 (1 SD); SI Table 2), compared to the PSW flow in western Fram Strait where the influence of Arctic waters resulted in lower log $K'_{Fe'L}$ values (the mean of log $K'_{Fe'L}$ 12.4±0.3 (1 SD); SI Table 2). The range in log $K'_{Fe'L}$ is relatively broad (Figure 6a), implying that different ligand sources supply ligands with various chemical properties, thus different affinity to bind Fe.

As detailed, organic ligands were present at higher concentrations near the glacier terminus and Westwind Trough than in the Norske Trough and Fram Strait (Figures 3b and 5a), but the ligands near the glacier terminus and Westwind Trough had a lower affinity for binding Fe (Figure 6a) and a lower competing strength, log $\alpha_{Fe'L}$ (Figure 6b). Krisch et al. (submitted) observed that glacial-derived Fe transfer through the Westwind Trough was low because of a net transfer of Fe from the colloidal (thus part of DFe) to the particulate phase with subsequent settling out of the water column, an important removal process in the Fe cycle (Wu et al., 2001). Although organic ligands exist in both the soluble and colloidal fractions (Boye et al., 2010; Fitzsimmons et al.,2015; Thuróczy et al., 2011), part of the colloidal Fe fraction is inert, and not exchangeable (Cullen et al., 2006) and might contribute to coagulation and aggregation and disappearance of Fe. We did not separate soluble and colloidal fractions, but we do demonstrate

that the ligands in the glacier outflow and Westwind Trough were relatively weak with a lower competing strength (Figures 6a and 6b). This results in a relatively high [Fe´] which in turn allow loss of DFe via precipitation and/or scavenging, consistent with the loss of colloidal Fe observed by Krisch et al. (submitted).

Global warming causes rapid environmental changes in the Arctic and sub-Arctic Oceans (Gascard et al., 2008; IPCC, 2014) to which Fram Strait belong (Ekwurzel et al., 2001; Schuur et al., 2015). These changes may alter the properties and distribution of organic Fe-binding ligands. Melting of sea-ice influences biological activity (Arrigo et al., 2008; Meier et al., 2014) and without considering possible nutrient depletion, this may increase the release of strong organic ligands. An increased competing strength of organic ligands enhances the ability of ligands to stabilize additional Fe input, potentially increasing the DFe export from Greenland towards the open ocean if the timing and location of DFe input coincides with the presence of these ligands. Not much is known about Fe limitation in the Nordic Seas, although potential Fe limitation was reported for the Nansen Basin of the Arctic Ocean (Rijkenberg et al., 2018). Also the Iceland Basin in the North Atlantic experiences seasonal Fe limitation (Hopwood et al., 2018; Mohamed et al., 2011; Nielsdóttir et al., 2009; Ryan-Keogh et al., 2013). Enhanced transport of ligand bound Fe from the Arctic may thus have a profound effect on primary productivity in the high-latitude North Atlantic. However, such changes must also be considered alongside other physical/chemical perturbations in the region as a result of ongoing changes such as the increase in freshwater discharge around Greenland. The complex interplay between Fe and ligand sources versus scavenging and coagulation will need to be better constrained to enable accurate predictions of changes in the biogeochemical cycle of Fe in the globally important northern high latitudes, as well as elsewhere.

Conclusion

This study provides a connection between the previous reports on organic Fe-binding ligands in the Arctic Ocean and North Atlantic Ocean, as well as insight into the competing strength of organic Fe-binding ligands that regulate DFe transport from a Greenland glacier. Our results indicate that the Fe-binding ligands in surface waters of Fram Strait originate from microbial activity with addition from southward-flowing TPD transported terrestrial ligands on the western side of Fram Strait. Given that the [L_t] in western Fram Strait is intermediate to the higher concentrations reported for the Arctic and the lower concentrations reported for the North Atlantic, this confirms the decreasing [L_t] southward from the Arctic Ocean.

In the Norske Trough, the remnant from an earlier bloom was likely the main source of organic Fe-binding ligands in surface waters, as the contribution of ligands can be substantial at the base of sea-ice. The elevated [L_t] at stations near the 79N Glacier terminus is probably associated with remineralization of glacially-derived organic matter. Our data shows that even though significantly higher concentrations of organic ligands were present at the vicinity of 79N Glacier terminus and in the Westwind Trough (outflow) than in the Norske Trough (inflow), the organic ligands are weaker and therefore can compete less efficiently with scavenging processes and precipitation. Especially close to the glacier, ligands have a weaker affinity for binding Fe. We show that transport of Fe in the glacial outflow is potentially regulated by ligands as has been anticipated from comparisons of particulate and dissolved Fe distributions in several systems worldwide. Additionally, our results reveal the underlying mechanism where the lower ligand binding strength and consequently higher [Fe´] (rather than a low concentration of ligands) result in more precipitation of Fe-oxyhydroxides or/and scavenging. Thereby only a small part of the glacial DFe will be transported over the shelf into the ocean. Different sources supply ligands with various chemical properties, resulting in distinctive properties of the ligand pool among regions.

Rapid environmental changes due to global warming will cause increased river runoff and glacial melt into the Arctic Ocean, increasing gross Fe supply into the Arctic basin. However, it is the combination of availability and binding strength of organic ligands that regulate DFe transport and distribution in Fram Strait region. Thus, to understand the consequences of global warming in the Arctic and sub-Arctic Oceans for the biogeochemical cycle of Fe, the changes in the biogeochemical cycle of the ligands need to be understood as well. Especially glacial systems will need to be investigated further to determine if there is strong temporal variability

575 in the concentration and competing strength of Fe-binding ligands or if large differences exist
576 between different glaciers.

Figure captions

- Figure 1. Map of the study area with schematic currents. The yellow marks indicate the station positions in this study sampled by a trace metal clean CTD Rosette sampling system. The blue dots indicate the stations sampled by a large CTD sampling system. The Fram Strait transect consists of stations 1, 7, 14 and 26. The northeast Greenland shelf transect consist of stations 17, 18 and 19 in the Norske Trough, stations 21 and 22 near the 79N Glacier terminus, and station 11 in the Westwind Trough. The West-Spitsbergen Current (WSC, indicated by red arrows) brings warm Atlantic Water (AW) into the Arctic Ocean. The southward flowing East Greenland (EGC, grey arrows) carries part of the recirculated WSC as well as outflow Polar Surface Water (PSW) from the Arctic Ocean. The yellow arrows indicate the anti-cyclonic circulation through the trough system. This figure is adapted from Schaffer et al., (2017) and based on Bourke et al., (1987).
- Figure 2. The distribution of absolute salinity (S_A), conservative temperature (Θ) and potential density (σ_θ) along the transects with the various water masses indicated. (a): Absolute salinity with potential density as contours in the Fram Strait transect; (b): conservative temperature with potential density as contours along the northeast Greenland shelf transect. The square symbol indicates the station (22) in front of the glacier terminus, and the dot symbol indicates the station (21) at ~20 km distance from the glacier terminus.
- Figure 3. The distribution of dissolved Fe (DFe, data from Krisch et al., submitted) and total Fe-binding ligand concentrations ($[L_t]$) of both transects; the Fram Strait transect on the left and the northeast Greenland shelf transect on the right. DFe concentrations (a,c) and $[L_t]$ (b,d). Along the northeast Greenland shelf transect, the square symbol indicates the station in front of the glacier terminus, and the dot symbol indicates the station at ~20 km distance from the glacier terminus.
- Figure 4. The distribution of ligand saturation ($[L_t]$/DFe) of both transects; the Fram Strait transect (a) and the northeast Greenland shelf transect (b). Along the northeast Greenland shelf transect, the square symbol indicates the station in front of the glacier terminus, and the dot symbol indicates the station at ~20 km distance from the glacier terminus.
- Figure 5. Boxplots of the concentrations of (a) total organic Fe-binding ligands, $[L_t]$, and (b) inorganic iron, [Fe´], from all stations in Fram Strait and over the northeast Greenland shelf (the Norske Trough and Westwind Trough), categorized by water mass. Indicated are the median value by a thick horizontal line, the box contains the first and third quartiles, the whiskers are the range of data excluding the outliers. The circles indicate the outliers being 1.5* interquartile range from the box (Teetor, 2011).
- Figure 6. Boxplots of the conditional stability constants (binding strength), log $K'_{Fe'L}$ (a) and side reaction coefficients (competing strength), log $\alpha_{Fe'L}$ (b) from all stations in Fram Strait and over the northeast Greenland shelf (the Norske Trough and Westwind Trough), categorized by water mass. The detail explanation of the boxplot is as described in Figure 5.

Supplementary Information (SI):

- SI Figure 1. The depth profiles of dissolved-Fe (DFe) and total ligand concentrations [L_t] for each station in Fram Strait and over the northeast Greenland shelf. Station numbers are indicated at the bottom right of each figure. Figures are made using the software package R.
- SI Figure 2. Boxplots of the total Fe-binding ligand concentrations, [L_t], from existing studies in the Arctic Ocean (Slagter et al., 2017; Thuróczy et al., 2011) and the North Atlantic Ocean (Gerringa et al., 2014). The letter "S" refers to surface data. Surface samples from Slagter et al., (2017) were selected from Polar Surface Water (PSW) at stations inside (81, 87, 91, 96) and outside (50, 64 and 69) the Transpolar Drift (TPD), based on the TPD definition as described in the original paper of Slagter et al., (2017). Surface samples from Thuróczy et al, (2011) were taken from upper 200m at stations in Makarov and Amundsen Basin. Surface samples from Gerringa et al., (2014) were taken from upper 200m at stations 2 and 5 in the North Atlantic Ocean.
- SI Table 1. Values for dissolved-Fe analyses of reference materials. The consensus values were obtained from http://www.geotraces.org/
- SI Table 2. The summary of ligand data grouped by water mass.
- SI Table 3. T-test statistics summary. The significance levels are $p<0.005$***, $p<0.01$**, $p<0.05$* and $p<0.1$

Acknowledgements
Authors would like to thanks Captain Schwarze and his crew of the RV Polarstern, as well as chief scientist Torsten Kanzow, for their effort and support during sample collection. Patrick Laan is acknowledged for analyzing DFe for Fe-binding ligands calculation. We thank anonymous reviewers for their comments that improved the manuscript considerably. IA was financed by Indonesia Endowment Fund for Education (LPDP), and SK was financed by GEOMAR and the German Research Foundation (DFG award number AC 217/1-1 to E. P. A). Figures 1 to 4 are made using the software Ocean Data View 5.1.7 (Schlitzer, 2018). Figures 5 and 6 are made using the software package R version 3.4.2. Data can be accessed online at https://doi.org/10.25850/nioz/7b.b.u.

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Fig.1

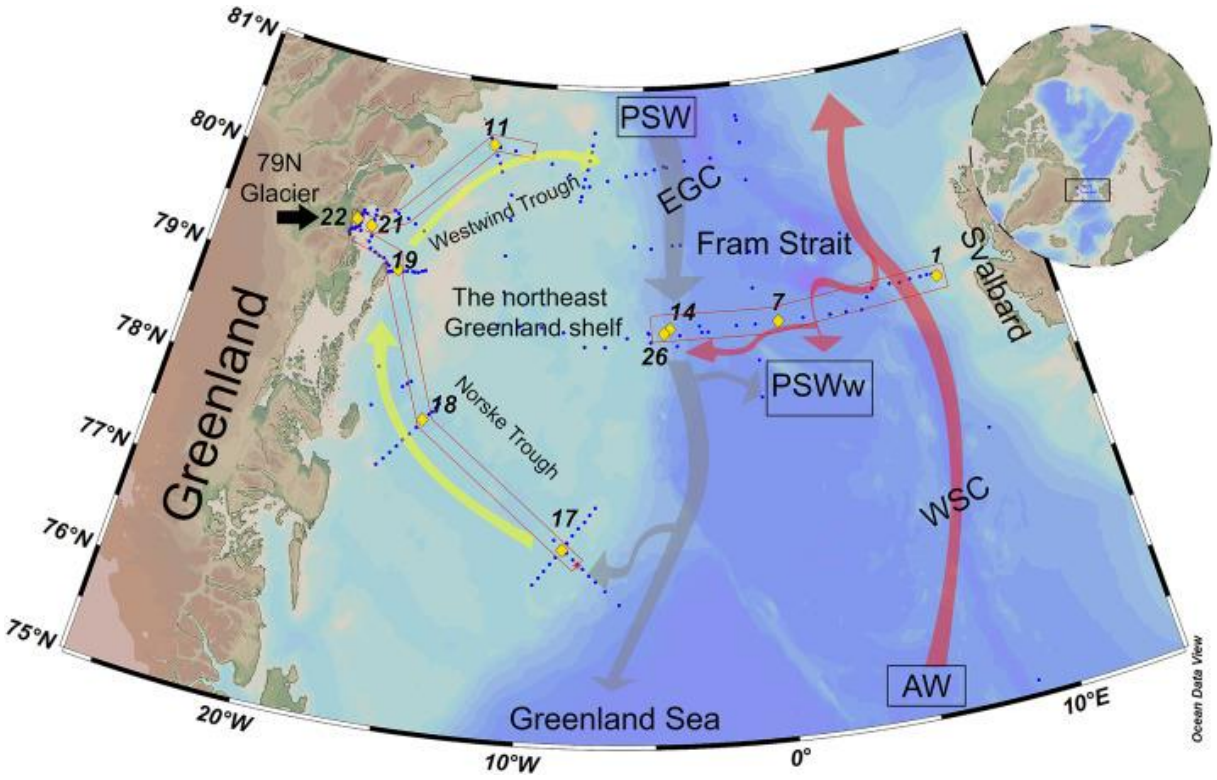


Fig. 2

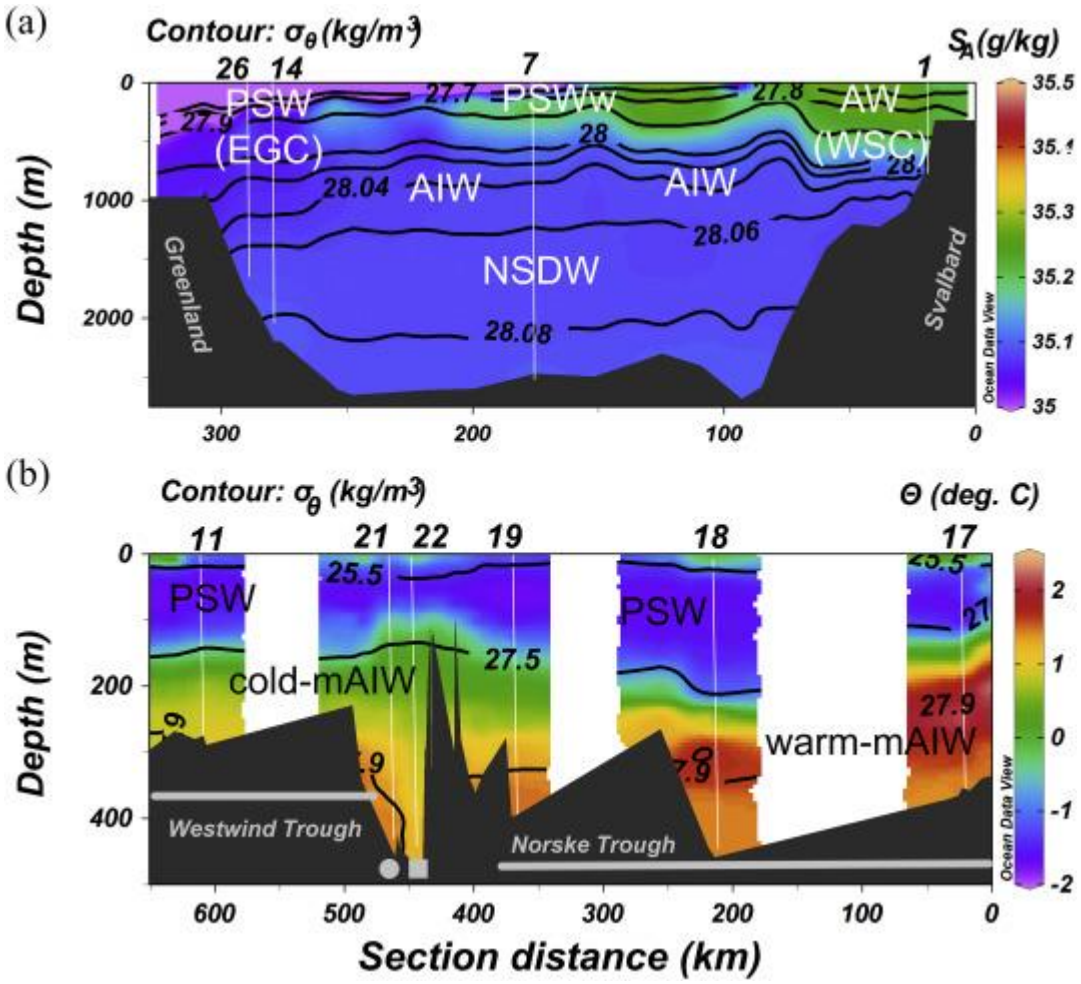

(a)
Contour: σθ (kg/m3)
SA (g/kg)
26 14
7
1
PSW
(EGC)
27.7
PSWw
27.8
AW
(WSC)
28
28.04
AIW
AIW
28.06
NSDW
28.08
Greenland
Svalbard
Depth (m)
0
1000
2000
300
200
100
0
Ocean Data View
35.5
35.3
35.2
35.1
35
(b)
Contour: σθ (kg/m3)
Θ (deg. C)
11
21
22
19
18
17
PSW
25.5
27.5
cold-mAIW
PSW
warm-mAIW
27.9
Westwind Trough
Norske Trough
Depth (m)
0
200
400
600
500
400
300
200
100
0
Section distance (km)
Ocean Data View
2
1
0
-1
-2

Fig. 3

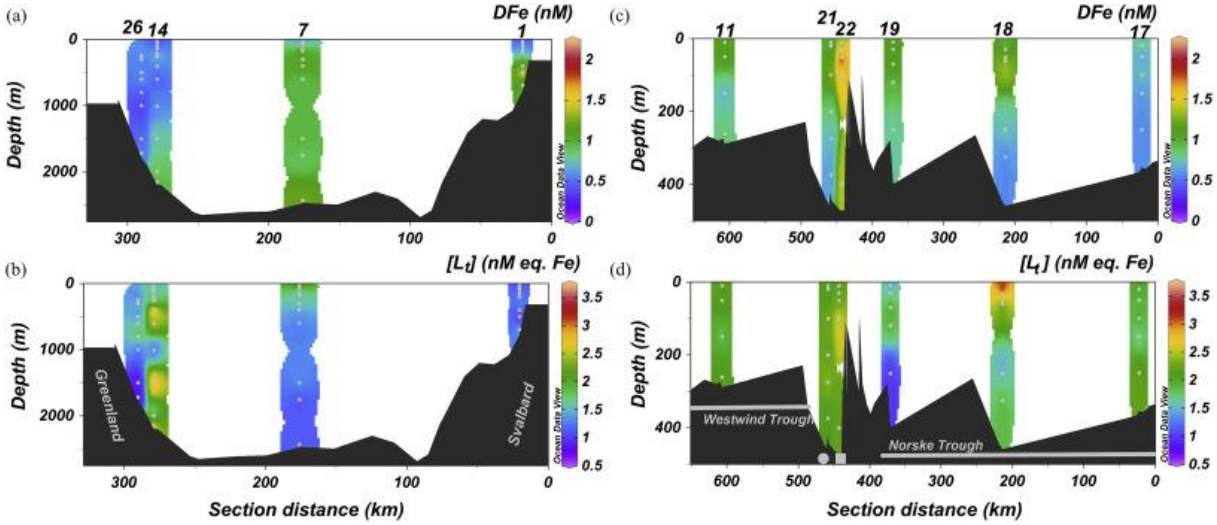

(a)
DFe (nM)
26 14
7
1
Depth (m)
0
1000
2000
300
200
100
0
(c)
DFe (nM)
11
21
22
19
18
17
Depth (m)
0
200
400
600
500
400
300
200
100
0
(b)
[Lt] (nM eq. Fe)
Greenland
Svalbard
Depth (m)
Section distance (km)
(d)
[Lt] (nM eq. Fe)
Westwind Trough
Norske Trough
Depth (m)
Section distance (km)
Ocean Data View

Fig. 4

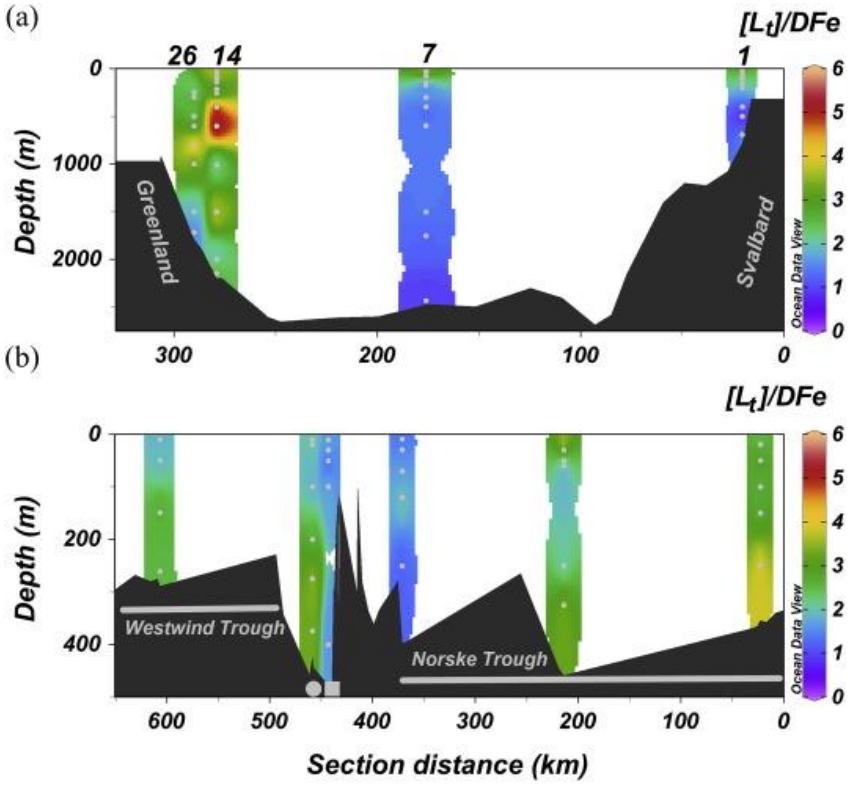

(a)
[Lt]/DFe
26 14
7
1
Depth (m)
0
1000
2000
Greenland
Svalbard
300
200
100
0
(b)
[Lt]/DFe
Depth (m)
0
200
400
Westwind Trough
Norske Trough
600
500
400
300
200
100
0
Section distance (km)
Ocean Data View

Fig. 5

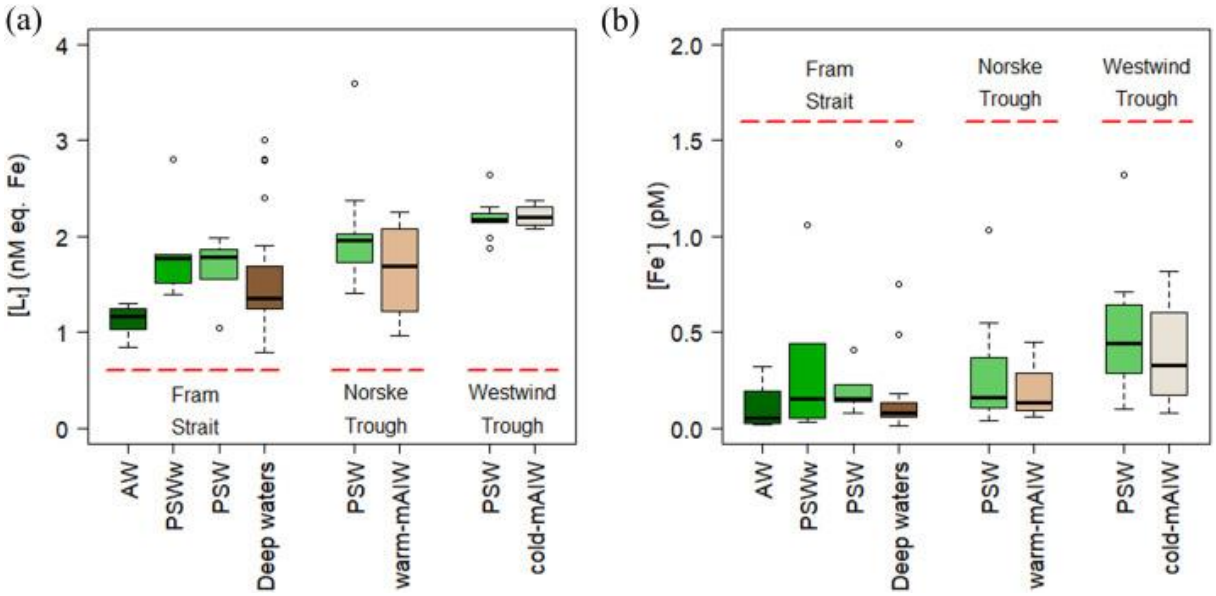
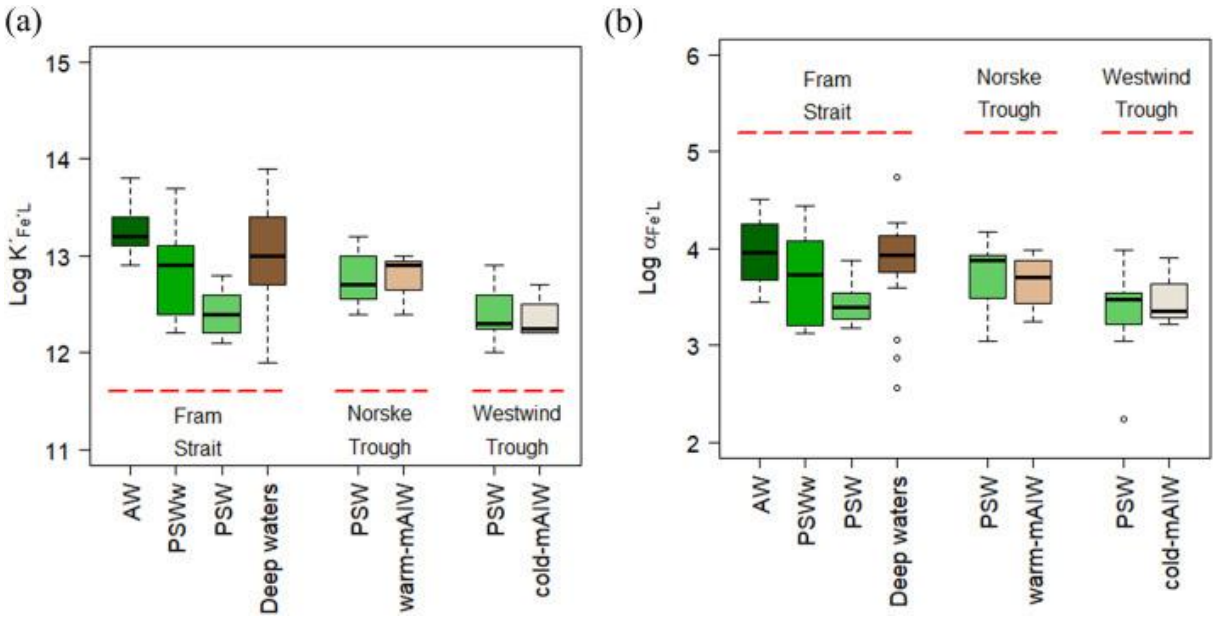

(a)
[L$_1$] (nM eq. Fe)
Fram Strait
Norske Trough
Westwind Trough
AW
PSWw
PSW
Deep waters
PSW
warm-mAIW
PSW
cold-mAIW
(b)
[Fe$'$] (pM)
Fram Strait
Norske Trough
Westwind Trough
AW
PSWw
PSW
Deep waters
PSW
warm-mAIW
PSW
cold-mAIW

Fig. 6


(a)
Log K$'_{Fe'L}$
Fram Strait
Norske Trough
Westwind Trough
AW
PSWw
PSW
Deep waters
PSW
warm-mAIW
PSW
cold-mAIW
(b)
Log $\alpha_{Fe'L}$
Fram Strait
Norske Trough
Westwind Trough
AW
PSWw
PSW
Deep waters
PSW
warm-mAIW
PSW
cold-mAIW

Supplementary Information (SI):
Data can be accessed at : https://doi.org/10.25850/nioz/7b.b.u

Table 1. Values for dissolved-Fe analyses of reference materials. The consensus values were obtained from http://www.geotraces.org/.

	Reference Material	Consensus value	Reported value
Entire PS100/GN05 trace metal samples analyses at GEOMAR	SAFe S (#273)	0.093 ± 0.008 nM	0.101 ± 0.016 nM (n = 10)
	GSP (#144, #192)	0.27 ± 0.05 nM	0.28 ± 0.07 nM (n = 11)
Dissolved-Fe samples from ligand bottles analyses at NIOZ	SAFe D1 (#169)	0.670 ± 0.04 nM	0.718 ± 0.024 nM (n = 3)

Table 2. The summary of ligand data grouped by water mass.

Province	Water mass		$[L_t]$ (nM eq. Fe)	log $K'_{Fe'L}$	[Fe´] (pM)	log $\alpha_{Fe'L}$	$[L_t]$/DFe
Fram Strait	AW	Mean	1.15	13.3	0.08	3.5	2.0
		SD	0.18	0.3	0.11	1.5	1.0
		N	8	8	7	8	8
		Median	1.20	13.3	0.05	4.0	2.0
	PSWw	Mean	1.84	12.9	0.31	3.7	2.4
		SD	0.50	0.6	0.39	0.5	1.2
		N	6	6	6	6	6
		Median	1.77	12.9	0.15	3.7	2.2
	PSW	Mean	1.63	12.6	0.18	3.6	3.1
		SD	0.33	0.5	0.13	0.4	1.0
		N	6	6	6	6	6
		Median	1.67	12.5	0.14	3.5	2.8
	deep waters	Mean	1.59	13.0	0.21	3.7	2.5
		SD	0.65	0.6	0.36	0.8	1.3
		N	20	20	19	20	20
		Median	1.36	13.0	0.08	3.9	2.1
Norske Trough	PSW	Mean	2.03	12.8	0.28	3.7	2.3
		SD	0.58	0.3	0.30	0.4	0.9
		N	11	11	11	11	11
		median	1.96	12.7	0.16	3.9	2.0
	warm-mAIW	Mean	1.65	12.8	0.11	3.7	2.6
		SD	0.55	0.3	0.04	0.3	1.3
		N	4	4	3	4	4
		Median	1.68	12.9	0.13	3.7	2.6
Westwind Trough	PSW	Mean	2.19	12.4	0.48	3.3	1.9
		SD	0.19	0.3	0.34	0.4	0.4
		N	11	11	10	11	11
		Median	2.17	12.3	0.41	3.5	1.9
	cold-mAIW	Mean	2.21	12.4	0.39	3.5	2.7
		SD	0.13	0.2	0.31	0.3	0.8
		N	4	4	4	4	4
		Median	2.20	12.3	0.33	3.4	2.9

Table 3. T-test statistics summary. The significance levels are p<0.005***, p<0.01**, p<0.05* and p<0.1.

		Parameters	P-value	
Fram Strait	AW vs PSW	$[L_t]$	0.03	*
		$\log K'_{FeL}$	**0.0009**	***
		$\log \alpha_{FeL}$	>0.1	
	AW vs PSWw	$[L_t]$	0.015	*
		$\log K'_{FeL}$	>0.1	
		$\log \alpha_{FeL}$	>0.1	
Northeast Greenland shelf	PSW in the Norske Trough vs. PSW in the Westwind Trough	$[L_t]$	0.008	**
		$\log K'_{FeL}$	0.009	**
		$\log \alpha_{FeL}$	0.032	*
	mAIW in the Norske Trough vs. mAIW in the Westwind Trough	$[L_t]$	0.095	
		$\log K'_{FeL}$	0.042	*
		$\log \alpha_{FeL}$	>0.1	

Note: the bold emphasis is mentioned in the discussion, and the others are provided as reference.

Fig. S1

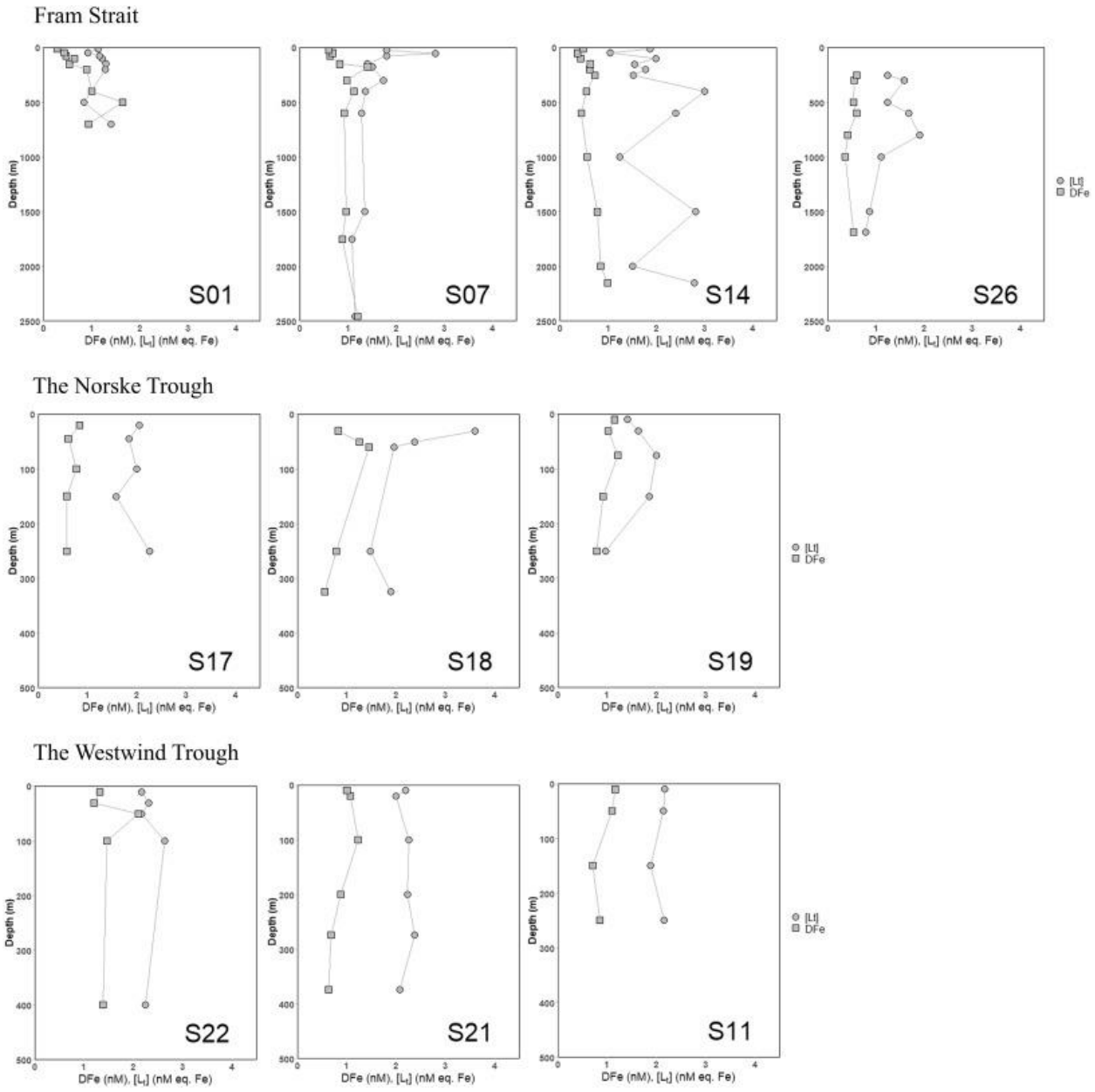
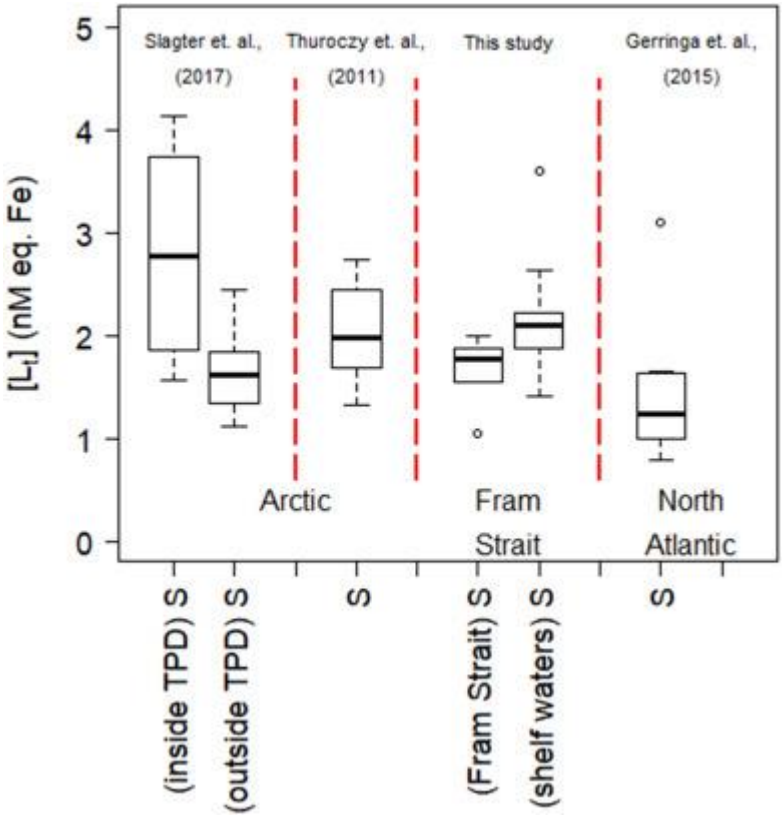

Fram Strait
S01
S07
S14
S26
The Norske Trough
S17
S18
S19
The Westwind Trough
S22
S21
S11
Depth (m)
DFe (nM), [Lt] (nM eq. Fe)
[Lt]
DFe

Fig. S2


Slagter et. al., (2017)
Thuroczy et. al., (2011)
This study
Gerringa et. al., (2015)
[L_t] (nM eq. Fe)
0
1
2
3
4
5
Arctic
Fram Strait
North Atlantic
(inside TPD) S
(outside TPD) S
S
(Fram Strait) S
(shelf waters) S
S