



1 **Organic matter as a driver of Fe(II) oxidation and** 2 **persistence in the central Arctic Ocean and the Barents** 3 **Sea: Implications for Marine Biogeochemistry**

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16 17 **Abstract**

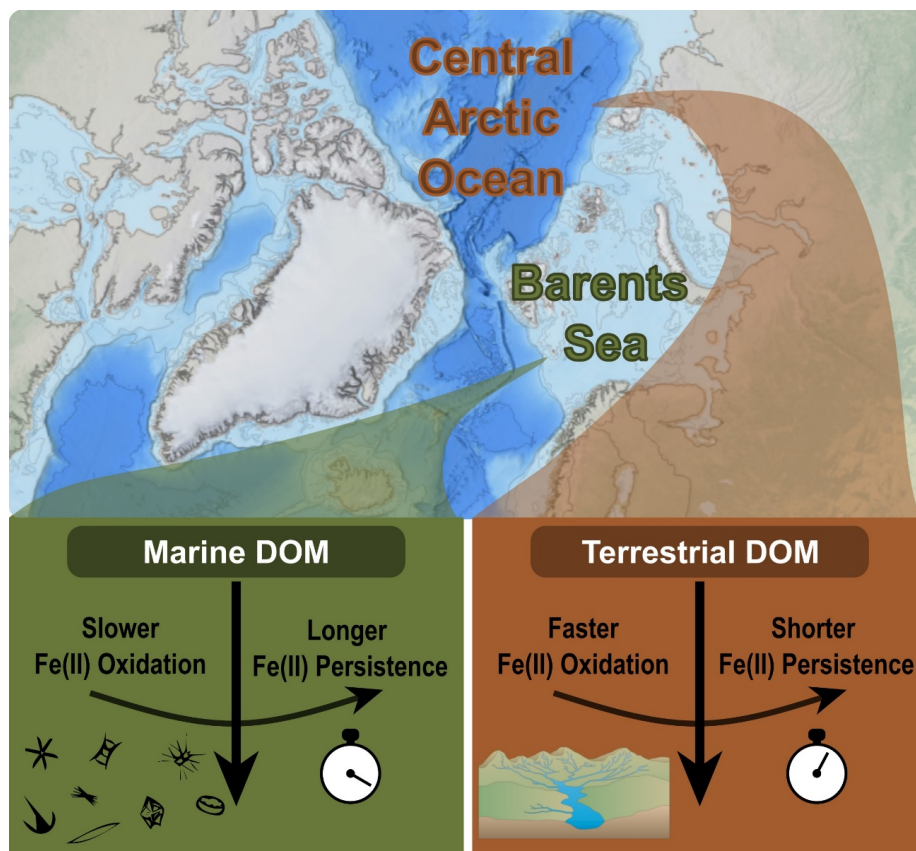
18 This study examines how variations in organic matter sources and composition regulate Fe(II) oxidation
19 dynamics in the central Arctic Ocean and the Barents Sea, two contrasting Arctic marine environments.
20 Pseudo-first-order Fe(II) oxidation rate constants ($\log k'$) deviated substantially from values predicted with
21 the same pH, temperature, and oxygen conditions, indicating strong environmental control on Fe(II)
22 reactivity. Under reference conditions (pH = 8, T = 15 °C, and oxygen saturation), the calculated Fe(II)
23 half-life was 14.21 min, whereas experimentally determined half-life ranged from 0.76 to 14.7 min in the
24 central Arctic Ocean and from 0.77 to 20.14 min in the Barents Sea. Experimental and calculated data
25 yielded a standard error in $\log k'$ of $\pm 0.229 \text{ min}^{-1}$, corresponding to a half-life uncertainty of less than 1
26 min. The Fe(II) half-life directly reflects oxidation kinetics and constrains Fe(II) persistence, with
27 implications for trace metal speciation and redox cycling.

28 Partial least squares regression (PLSR) analysis of samples from the Central Arctic station revealed
29 significant associations ($R^2 = 0.38$, $p < 0.05$) between residual Fe(II) oxidation variability ($\Delta k'$) and humic-
30 like organic matter, dissolved organic carbon (DOC), silicic acid, salinity, and nitrate, highlighting the
31 combined influence of interrelated environmental factors on Fe(II) oxidation dynamics. Spatial variability
32 in Fe(II) persistence across basins and depth profiles is attributed to differences in organic matter
33 characteristics associated with distinct water masses.



34 Graphical Abstract

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40 1. Introduction

41 The oceanographic characteristics of the Arctic Ocean are influenced by the interaction of Atlantic and
42 Pacific water inflows, combined with substantial freshwater input from major river systems and sea-ice
43 formation and melt. These inputs result in a vertically stratified water column, with a cold, low-salinity
44 surface layer overlying a warmer, saltier intermediate layer (Rudels, 2015). This structure exerts a critical
45 influence on the sea-ice dynamics, the seasonal thermohaline processes and the distribution of inorganic
46 and organic compounds. Due to limited exchange with the Atlantic and Pacific oceans and the significant
47 presence of allochthonous dissolved organic matter (DOMt) from terrestrial sources, the central Arctic
48 represents an area of high biogeochemical relevance (Williford et al., 2022). However, regional variations
49 exist within the Arctic Ocean, with areas such as the Barent Sea exhibiting distinct hydrographic and
50 biogeochemical characteristics as an Arctic inflow shelf (Carmack and Wassmann, 2006). The Barents Sea
51 is a shallow shelf sea, whose waters are shaped by the large inflow of warm, saline Atlantic water (AW)
52 from the Norwegian Sea interacting with cold Arctic waters and sea ice. It exhibits relatively high salinity
53 and oxygen levels due to its strong mixing and AW inflow, which prevents permanent ice cover and
54 maintains active circulation (Rudels, 2015). Unlike other Arctic shelf areas, it receives limited river runoff,
55 and thus is low in DOMt (Sandven et al., 2023). The combination of physical conditions (relatively warm
56 Atlantic currents, seasonal sea-ice dynamics, nutrient-rich waters, and prolonged summer daylight)
57 supports intense biological activity, making the Barents Sea one of the most biologically productive shelf
58 seas in the Arctic (Carmack and Wassmann, 2006; Rudels, 2015; Wassmann et al., 2006). High nutrient
59 availability sustains rich marine ecosystems in the region producing autochthonous dissolved organic
60 matter (DOMm). These environmental contrasts across the Arctic Ocean provide a valuable natural
61 laboratory for assessing how the origin of dissolved organic matter (DOM) influences the oxidation kinetics
62 and persistence of Fe(II) in the marine environment. In the ocean, Fe(II) is the soluble form of iron and
63 tends to be oxidized to Fe(III) which is less soluble and removed from solution (Liu and Millero, 2002;
64 Millero et al., 1987). Oxidation happens on different time scales influenced by several factors (pH,
65 temperature, salinity, DOM, particles and colloids) resulting in varying half-life estimates for Fe(II).
66 In artificial seawater or a seawater solution with low DOM content, the persistence of Fe(II) (half-life, $t_{1/2}$,
67 min) is controlled by the O_2 concentration, the pH, temperature and salinity (Santana-Casiano et al., 2005).
68 Under O_2 saturated conditions, Fe(II) oxidation rate constant (k'_{cal} , s^{-1}) is calculated as a function of pH,
69 temperature, and salinity over a broad oceanic range (González-Santana et al., 2021). However, coastal and
70 oceanic seawater are influenced by multiple sources and processes that generate DOM with different
71 composition and concentration. Consequently, the presence of DOM in seawater affects the Fe(II) oxidation
72 rate constant as stated several decades ago (Millero and Sotolongo, 1989; Rose and Waite, 2002, 2003a;
73 Santana-Casiano et al., 2000).
74 Studies using individual organic compounds attempt to provide answers and insights into the persistence
75 of Fe(II) in the marine environment. Laboratory studies show that individual organic compounds can either
76 speed up or slow down the oxidation kinetic rate of the Fe(II) (Pham and Waite, 2008; Santana-Casiano et
77 al., 2000; Theis and Singer, 1974). The effect that organic compounds have on Fe(II) regeneration through
78 abiotic Fe(III) reduction processes has also been the subject of attention, where the type and functional
79 groups of the organic compounds are key to the process (Arreguin et al., 2021; González et al., 2019; Pérez-



Almeida et al., 2022; Santana-Casiano et al., 2010, 2014). Studies using environmental samples show that the source of DOM can significantly influence Fe(II) oxidation kinetics (Lee et al., 2017a; Rose and Waite, 2002, 2003b; Roy and Wells, 2011; Santana-González et al., 2018, 2019). The Fe(II) oxidation rates for freshwater are higher than those for coastal waters. The presence of humic-like DOMt tends to accelerate the Fe(II) oxidation in freshwater (Lee et al., 2017a, b). However, protein-like DOM from phytoplankton and microbial derived DOM tends to decrease the oxidation rates in seawater (González et al., 2012, 2014; Lee et al., 2017b; Samperio-Ramos et al., 2016, 2017). The lower oxidation rates for Fe(II) in coastal seawater compared with freshwater and organic ligand-free seawater is due to the presence of DOM of different characteristic. The k' variability observed in the presence of different organic compounds suggests that the effect of DOM on Fe(II) oxidation is dependent on the type of organic molecules (functional groups) and their complexing and redox properties (Lee et al., 2017a, b; Santana-Casiano et al., 2022). Information on Fe(II) oxidation rate and therefore $t_{1/2}$ in the ocean is essential for global biogeochemical models (Tagliabue and Völker, 2011).

Iron biogeochemistry in the Arctic Ocean and Barents Sea has been studied in relation to its sources, speciation, organic complexation, and role in primary productivity (Charette et al., 2020; Klunder et al., 2012a; Rijkenberg et al., 2018; Slagter et al., 2017, 2019). However, Fe(II) oxidation kinetics have not yet been investigated in these Arctic regions, representing an important knowledge gap in understanding Fe persistence and bioavailability.

This work aimed to study the Fe(II) oxidation kinetic constants in the central Arctic Ocean and Barents Sea to identify possible factors associated with DOM composition and origin that can help explaining the varying stability of Fe(II) in the marine environment. The rate constants ($\log k'$) and half-life times ($t_{1/2}$) for Fe(II) oxidation are presented at a fixed pH and temperature, allowing the identification of non pH and temperature effects on the Fe(II) oxidation rate constants in the Barents Sea and central Arctic Ocean.

2. Material and Methods

2.1 Description of the area of study

To better understand how organic matter influences Fe(II) persistence under different environmental conditions, we compare two Arctic regions with distinct physical and biogeochemical characteristics: the central Arctic Ocean and the Barents Sea (Fig. 1).

The Arctic has two major basins, the Eurasian and Amerasian Basins, which are separated by the Lomonosov Ridge (Rudels, 2015). The Eurasian Basin is divided into the Nansen and Amundsen Basins by the Gakkel Ridge. The Amerasian Basin is divided by the Alpha-Mendeleev Ridge into the Canada Basin and the Makarov Basin (Charette et al., 2020). Surrounding these basins are shallow and wide continental shelves (Jakobsson, 2002). AW flows into the Arctic through the Barents Sea and the Fram Strait, while Pacific water enters through the Bering Strait (Rudels, 2015). The Arctic waters flow through the Canadian Arctic Archipelago and the Fram Strait into the North Atlantic (Carmack et al., 2016). The Makarov, Nansen and Amundsen Basins are influenced by AW inflow and the fluvial discharge of the Siberian rivers with high concentration of DOMt (Williford et al., 2022). The Transpolar Drift (TPD) is a current that connects the Eurasian shelves to the Fram Strait and transports terrestrial material including DOMt from the Siberian shelves toward the North Atlantic (Charette et al., 2020; Williford et al., 2022).



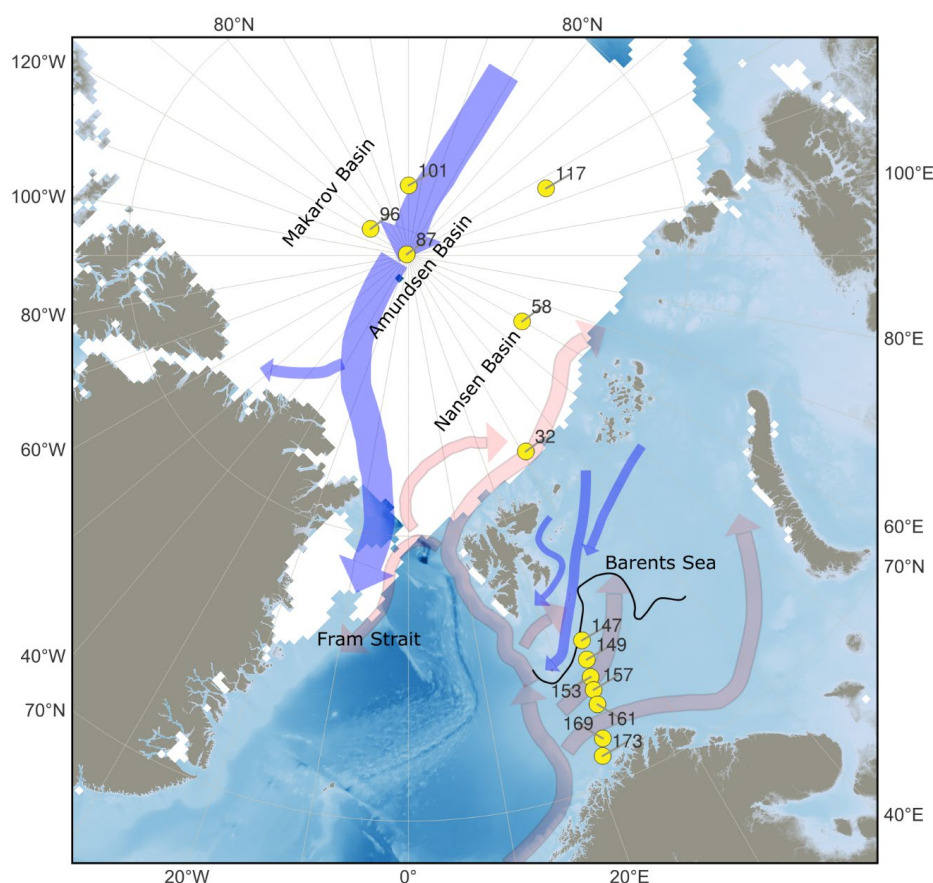
120 The path of the TPD crosses two of three basins beyond the Siberian continental plane, the Amundsen and
121 Makarov (Arnone et al., 2023; Slagter et al., 2017, 2019) enriching them with material of fluvial origin.
122 Arctic rivers are an important source of DOMt and dissolved trace metals on the shelves and in the central
123 Arctic Ocean (Arnone et al., 2023; Charette et al., 2020; Klunder et al., 2012b; Rijkenberg et al., 2018;
124 Slagter et al., 2017, 2019; Williford et al., 2022).

125 The Barents Sea is a relatively shallow continental shelf, with an average depth of 230 m and a maximum
126 depth of 500 m in the western channel (Loeng, 1991). It is notably influenced by AW inflow, limited
127 riverine influence (Rudels, 2012; Sandven et al., 2023), and is characterized as an inflow shelf (Carmack
128 and Wassmann, 2006). In the southern Barents Sea, currents flow eastward, while to the north, they move
129 westward or southwestward (Loeng, 1991). The extent of polar water in the Barents Sea is influenced by
130 favorable wind conditions, which affect both the magnitude of the inflow and the exchange with AW
131 (Strzelewicz et al., 2022; Walczowski et al., 2017) and influx of sea ice (Lind et al., 2018). The Polar Front
132 in the Barents Sea (Fig. 1) marks the boundary between the warmer and saltier AW to the south and the
133 colder and less saline Arctic Water to the north, characterized by sharp gradients in both temperature and
134 salinity (Kolodziejczyk et al., 2025).

135

136 **2.2 Sampling**

137 The samples were collected in the framework of the GEOTRACES program during the TransArc II
138 expedition on the R/V Polarstern to the Arctic Ocean (PS94, ARK-XXIX/3, GEOTRACES transect GN04)
139 from 17 August to 15 October 2015 (Schauer, 2016). This study focuses on the stations shown in Fig. 1.
140 For the Fe(II) kinetics studies, a total of 6 stations were sampled in the Arctic Ocean and 7 in the Barents
141 Sea. Stations numbers in the central Arctic Ocean were 96 and 101 (Makarov Basin), 87 and 117
142 (Amundsen Basin), and 58 and 32 (Nansen Basin), the latter close to Svalbard continental slope. All stations
143 in the Barents Sea were south of the Polar Front (stations 147, 148, 149, 150, 151, 169 and 173, see Fig. 1).
144 The samples for iron were collected from an ultra-clean CTD (UCCTD) rosette (Rijkenberg et al., 2018),
145 following the GEOTRACES protocols (Cutter et al., 2017), in an ISO Class 6 clean room container. All the
146 samples were filtered by 0.2 μm Sartobran 300 cartridges (Sartorius), under pressure of filtered N_2 (0.7
147 bar). The samples were collected in 125 mL low-density polyethylene (LDPE) bottles after rinsing 3 times
148 with seawater before filling and stored at -20°C until analysis.



149

150 Figure 1. Map of stations (yellow circles) sampled in the central Arctic Ocean and the Barents Sea for Fe(II)
 151 studies. Sea ice extent is from 23rd Aug 2025 (the date station 32 was visited) based on data from the
 152 University of Bremen (Spreen et al., 2008). Wide blue arrows indicate the approximate location of the
 153 Transpolar Drift current. Red arrows indicate major pathways of Atlantic water into the region. The blue
 154 arrows in northern Barents Sea indicate surface flow of colder Arctic waters, and the solid black line is the
 155 approximate position of the Polar Front (Gerland et al., 2023).

156

157 2.3 Oxidation kinetic experiments

158 The kinetic experiments for Fe(II) oxidation were conducted in a 60 mL LDPE container inside a double-
 159 walled, glass, thermo-regulated cell connected to a thermostatic bath (Julabo™), as described in previous
 160 studies (Santana-González et al., 2018, 2019). All the experiments were carried out in saturated O₂
 161 conditions. Moreover, experiments were performed in the dark to avoid the generation of additional reactive
 162 oxygen species (ROS) from photo-oxidation processes and the photo-transformation of Fe.



For each oxidation kinetic study, 25 mL of seawater sample was used. The initial concentration of added Fe(II) was 0.97 nM. Previous studies have shown that the inorganic Fe(II) oxidation rate constant is independent of the added Fe(II) concentration (Millero et al., 1987; Santana-González et al., 2017). As the rate of Fe(II) oxidation kinetics is influenced by pH and temperature, the kinetic experiments for the different stations and depths were carried out at a free scale pH of 8 and a temperature of 15°C, thereby allowing for comparison between them. Moreover, experiments were also conducted at a fixed pH of 8.0 at temperatures of 4, 7, 10, and 15 °C to determine the temperature dependence. Similarly, experiments at fixed temperatures of 4 and 15 °C with pH values of 7.8, 8.0, and 8.1, to assess the pH dependence, were performed.

During each oxidation kinetic experiment, the air bubbled samples kept regulated pH by using a Titrino 719 (Metrohm™), which automatically dispensed 0.01 M hydrochloric acid (HCl, PANREAC Hiperpur-plus). The pH electrodes were calibrated using a Tris buffer solution (Millero, 1986).

The total dissolved Fe(II) (TdFe(II)) concentration in the samples for the kinetic experiments was measured using the Flow Injection Analysis by chemiluminescence (FIA-CL) technique with a FeLume system (Waterville Analytical) (King et al., 1995), as previously described (González-Santana et al., 2021; Santana-Casiano et al., 2022). The FIA-CL technique uses luminol as reagent. Luminol reagent (5 L) was prepared using 2.71×10^{-4} M of 5-amino-2,3-dihydro-1,4-phthalazinedione (Sigma), 4.93×10^{-2} M of Na_2CO_3 (Sigma-Aldrich) and 0.4 M of previously distilled 25% NH_3 (Panreac). The final pH was adjusted to 10.4 by adding 0.06 M Q-HCl. The luminol solution was stored in the dark to prevent degradation due to light exposure.

183

2.4 Determination of rate constants and half-life

Fe(II) oxidation kinetic studies in different aqueous media and conditions (Millero et al., 1987; Rose and Waite, 2002; Santana-Casiano et al., 2022; Stumm and Lee, 1961) have shown that the rate of oxidation with O_2 can be expressed as an apparent rate constant (k_{app}), regardless of the mechanism that describes the process (Eq. 1).

$$\frac{d[\text{Fe(II)}]}{dt} = -k_{app}[\text{Fe(II)}][\text{O}_2] \quad (1)$$

$$k_{app} = \sum_i k_i \cdot \alpha_i + \sum_j k_{Lj} \cdot \alpha_{FeLj} \quad (2)$$

where α_i is the fraction of each inorganic Fe(II) species in the solution with a rate constant k_i and α_{FeLj} are the fraction of different Fe(II)-organic ligands complexes in the solution, with a rate constant k_{Lj} .

When the reaction is studied in saturated O_2 conditions, the reaction can be considered pseudo-first order (Eq. 3).

$$\frac{d[\text{Fe(II)}]}{dt} = -k'[\text{Fe(II)}] \quad (3)$$

where $k' = k_{app} [\text{O}_2]$ expressed in min^{-1} , and k_{app} is expressed in $\text{M}^{-1} \text{min}^{-1}$. The slope corresponding to the plot of $\ln [\text{Fe(II)}]$ vs time determines the k' (min^{-1}). The half-life time is obtained from

$$t_{1/2} = \frac{\ln 2}{k'} \quad (4)$$

The calculated k'_{cal} (s^{-1}) value (Eq. 5) is obtained from an empirical equation (González-Santana et al., 2020) for known conditions of temperature, pH, and salinity (S). This equation is valid from 0.5 nM to 200 nM of Fe(II) (González-Santana et al., 2021).



$$\log(k'_{cal}) = 35.627 - 6.7109 \times pH + 0.5342 \times pH^2 - \frac{5434.02}{T} - 0.04406 \times \sqrt{S} - 0.002847 \times S \quad (5)$$

To compare calculated values with experimentally measured values, all of them are expressed in minutes. Experimental data and the theoretically derived data (k'_{cal}) had a standard error of estimate in $\log k'$ of ± 0.229 (k' in min^{-1}), which corresponds to a half-life error of less than 1 min.

2.5 FDOM data

The fluorescent dissolved organic matter (FDOM) characterization used in this study was partially reported previously (Williford et al., 2022). Briefly, for FDOM, excitation-emission matrices (EEMs) were modelled using Parallel Factor Analysis (PARAFAC) to identify distinct fluorescent components of DOM. For the EEMs, a six-component model (C) was optimized based on spectral loadings, residual examination, and split-half validation using a convergence criterion of $1e^{-8}$ (Williford et al., 2022). The components were labelled based on their emission maxima: C₄₉₂, C₄₅₆, C₄₁₁, C₄₀₄, C₃₃₈, and C₃₀₂. The resulting components were grouped into humic-like material, from terrestrial signature (C₄₉₂, C₄₅₆, C₄₁₁, C₄₀₄), and protein-like material, from fresh marine signature (C₃₃₈, C₃₀₂) based on their spectral signatures and previously reported assignments (Williford et al., 2022). PARAFAC components provide insight into the molecular character and origin of DOM fractions that influence trace metal complexation, solubility, and transport.

2.6 Lignin phenol data

The lignin phenol data used in this study in relation to Fe(II) oxidation data were partially reported previously (Williford et al., 2022). Briefly, terrigenous biomarkers were measured following the CuO oxidation and UHPLC-QqQ-MS detection procedures detailed in Yan and Kaiser (2018). Eleven dissolved lignin phenol monomers (in nM L^{-1}) were quantified: p-hydroxybenzaldehyde (PAL), p-hydroxyacetophenone (PON), p-hydroxybenzoic acid (PAD), vanillin (VAL), acetovanillone (VON), vanillic acid (VAD), syringaldehyde (SAL), acetosyringone (SON), syringic acid (SAD), p-coumaric acid (CAD), ferulic acid (FAD). Added together (except CAD + FAD) 9 lignin phenol monomers make up the total lignin phenol concentration presented in this study. Lignin phenols have served as robust tracers of terrigenous organic matter inputs in the Arctic Ocean (Amon et al. 2024) that are key to understanding metal-ligand interactions in Arctic waters (Williford et al. 2021) but one needs to be aware that lignin phenols only make up about 1% of the total terrigenous DOC found in rivers.

2.7 Statistical analysis of residual Fe(II) oxidation variability

To investigate the environmental factors associated with deviations between experimental and theoretically predicted Fe(II) oxidation kinetics, a partial least squares regression (PLSR) analysis was performed. The response variable was defined as:

$$\Delta k' = k'_{obs} - k'_{cal} \quad (6)$$

where k'_{obs} is the experimentally determined pseudo-first-order Fe(II) oxidation rate constant, and k'_{cal} is the oxidation rate constant predicted (Eq. 5) from established abiotic controls, considering pH, temperature, and salinity (González-Santana et al., 2020). This residual term therefore represents the fraction of Fe(II) oxidation variability not explained by conventional physicochemical predictors.



PLSR was selected because several environmental predictor variables exhibited strong collinearity, making ordinary multiple regression unsuitable. Predictor variables were selected to represent hydrographic conditions, nutrient distributions, dissolved organic matter (DOM), and optical properties potentially associated with reactive ligand pools. Specifically, the model included salinity (S) and pressure (Press) as hydrographic descriptors; nitrate (NO_3^-), phosphate (PO_4^{3-}), and silicic acid ($\text{Si}(\text{OH})_4$) as nutrient tracers; dissolved organic carbon (DOC) as a bulk DOM indicator, and fluorescence-derived optical proxies (C_{456} and C_{338}) representing different DOM characteristics.

All predictor variables were standardized to zero mean and unit variance prior to analysis. Observations containing missing values were excluded. The optimal number of latent PLS components was determined using 10-fold cross-validation by minimizing the mean squared prediction error. Variable importance was assessed using Variable Importance in Projection (VIP) scores, with $\text{VIP} > 1$ considered indicative of influential predictors. To complement the multivariate analysis, Pearson correlation coefficients (R) between $\Delta k'$ and each predictor variable were also calculated.

3. Results

3.1 Thermodynamic and pH effects on the Fe(II) reaction kinetics

Surface water (15 m) of station 87 in the Amundsen Basin (North Pole) was selected to study the dependence of $\log k'$ on both pH and temperature. The $\log k'_{\text{obs}}$ obtained were compared with $\log k'_{\text{cal}}$.

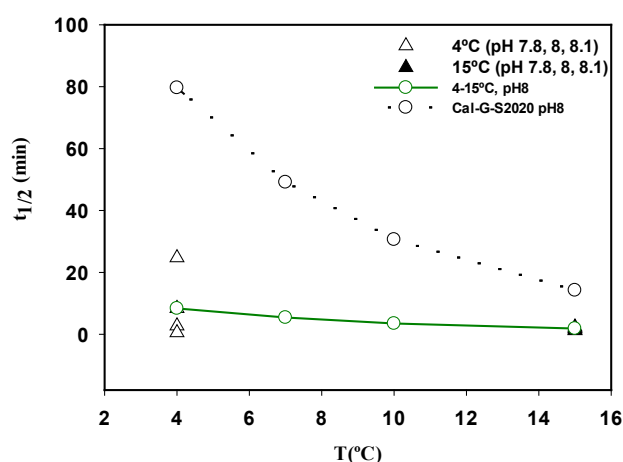
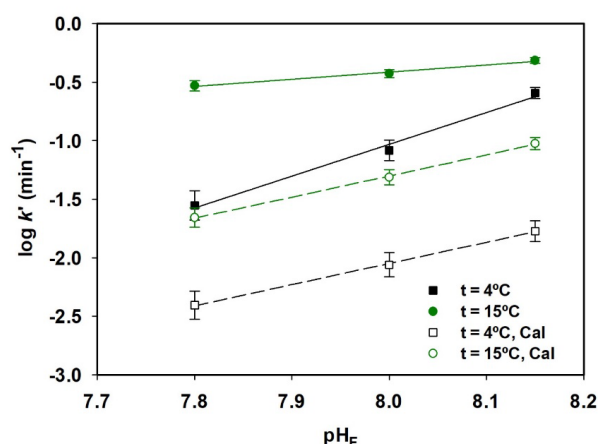
Fig. 2A shows the dependence of $\log k'$ on pH (7.8, 8 and 8.1) at temperature (4°C and 15°C), compared with $\log k'_{\text{cal}}$, all expressed in min^{-1} . At 15°C , even when $\log k'$ are different, the calculated and experimental slopes are close ($p < 0.05$). However, the slope changes in relation to the calculated values at 4°C , indicating that temperature may play an important role in the interaction of Fe(II) with the organic components.

Fig. 2B shows the $t_{1/2}$ obtained at pH 8 for different temperatures (4, 7, 10 and 15°C) and the comparison with the calculated values (González-Santana et al. 2021). The $t_{1/2}$ data at 4°C and 15°C for different pH (7.8, 8.0, 8.1 and 8.3) were also included. In all cases the experimental $t_{1/2}$ values are shorter than the theoretical one. At 15°C , a decrease from the expected value of 24.21 min to 1.8 min (93 %) is obtained, and at 4°C from 79.64 min to 8.36 min (90 %). This indicates that the kinetics are faster than expected at a fixed temperature. This agrees with previous studies (Santana-González et al., 2018; 2019) in the subarctic area (Irminger Sea and Labrador), where it was found that in surface and coastal waters, organic compounds measured as total organic carbon (TOC) accelerated k' , decreasing the Fe(II) half-life. It is important to highlight that station 87 is in a region affected by the TPD (Arnóne et al., 2023; Charette et al., 2020; Slagter et al., 2017) in surface waters, where substantial quantities of allochthonous material have frequently been observed (Charette et al., 2020; Williford et al., 2021, 2022). Unfortunately, no samples were taken at this station to characterise DOM, but in situ measurement of FDOM fluorescence was elevated in surface waters at neighboring stations (Rabe et al., 2016).

Using the Arrhenius equation at a constant pH of 8, the activation energy of the process was obtained when $\log k'$ was represented versus $1/T$ ($^\circ\text{K}$). The value of the slope was 4760.2 ± 150 and the $E_a = 91.13 \pm 3 \text{ kJ mol}^{-1}$. This value is slightly lower than the E_a from Gulf Stream water (slope 5362 ± 162 , and E_a of $103 \pm 3 \text{ kJ mol}^{-1}$; Santana-Casiano et al., 2005) and Central North Atlantic Region (slope 5434 ± 183 , $E_a = 104 \pm 3 \text{ kJ mol}^{-1}$ González-Santana et al., 2021). However, the Arctic Ocean E_a values are similar to those in the



282 Labrador Sea, that had a range from $89 \pm 1 \text{ kJ mol}^{-1}$ in surface waters to $80 \pm 1 \text{ kJ mol}^{-1}$ in deep waters at pH
283 8 (Santana-González et al., 2019). Previous studies in the subarctic area in the Irminger and Labrador seas
284 (Santana-González et al., 2018, 2019) have shown that in natural conditions, temperature was the master
285 variable which controlled 75% of k' , also suggesting that the sources and characteristics of organic matter
286 could affect the Fe(II) oxidation rate.



288 Figure 2 (A) Relationship of $\log k'$ with pH values (7.8, 8.0, and 8.1) at two temperatures (4°C and 15°C)
289 for station 87 (solid lines) and comparison with $\log k_{\text{cal}}$ (dashed lines), all expressed in min⁻¹. (B) The half-
290 life ($t_{1/2}$) obtained at pH 8 for different temperatures (4°C , 7°C , 10°C and 15°C) for station 87 and comparison with
291 the calculated values using Equation 5.
292

293 294 3.2 Station-based comparison of Fe(II) oxidation kinetics

295 The Fe(II) oxidation kinetics in the central Arctic Ocean and the Barents Sea, exhibited significant variation
296 in Fe(II) half-life (Fig 3A, 3B and 4). The $t_{1/2}$ at pH=8, $T=15^\circ\text{C}$ and saturated oxygen conditions changed
297 from 0.76 min in the surface waters of the Makarov Basin to 14.7 min in the intermediate waters of the



298 same basin. In the Barents Sea $t_{1/2}$ ranges from 0.77 to 20.14 min were obtained. These variations are not
299 attributable to changes in O_2 concentration, pH, or temperature, as these variables were maintained constant
300 during the experiments. At fixed pH and temperature for all experiments the calculated $t_{1/2}$ value (Eq. 5) is
301 $t_{1/2cal} = 14.21$ min.

302 Since these two regions are influenced by different DOM sources, distinct hydrographic regimes and water
303 masses, they will be examined independently.

304

305 **3.2.1 Central Arctic Ocean**

306 For the central Arctic waters, Fig. 3A shows the $t_{1/2}$ at different depths in the upper 100 meters for the
307 stations in the Makarov Basin (101, 96), the Amundsen Basin (117, 87) and the Nansen Basin (58, 32).

308 Differences in $t_{1/2}$ between basins were observed in surface waters down to 100 m. In the Makarov and
309 Amundsen Basins, $t_{1/2}$ is shorter than in the Nansen Basin, indicating a higher acceleration in the Fe(II)
310 oxidation rate constant compared to the Nansen Basin. Station 117 is at the border between the Amundsen
311 and Nansen basins and the $t_{1/2}$ values in subsurface waters are closer to those of station 58 in the central
312 Nansen Basin. Station 32, on the Svalbard slope in the AW inflow, had shorter $t_{1/2}$ compared to stations 58
313 and 117. In general, $t_{1/2} < t_{1/2cal}$ with values 93% shorter than the theoretical one, due to rapid disappearance
314 of Fe(II).

315 The position of each station in this area of complex hydrography is key to understanding the differences in
316 $t_{1/2}$ because this will also affect DOM composition, which conditions the interaction of Fe(II) with organic
317 matter.

318 In intermediate waters (500-1000 m) the situation changed (Fig. 3B). In the Makarov Basin, $t_{1/2}$ was higher
319 and similar to $t_{1/2cal}$. In the Amundsen and Nansen Basins the $t_{1/2}$ values are still shorter and nearly half of
320 the calculated ones. Station 117 shows the greatest variability throughout the column, with the highest
321 values in the deepest waters.

322 In deeper waters, the decrease in $t_{1/2}$ is observed to be higher in the Amundsen and Nansen Basins,
323 indicating spatial variability in oxidation kinetics.

324

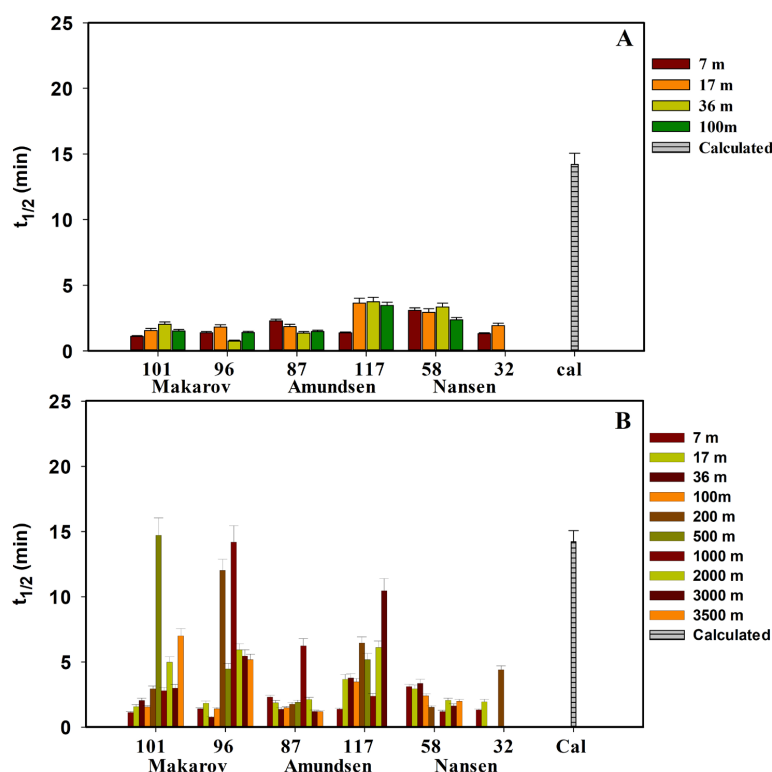


Figure 3. The Fe(II) half-life ($t_{1/2}$) at (A) various depths in the upper 100 meters and (B) at all the vertical profiles for two stations in the Makarov Basin (101, 96), two in the Amundsen Basin (87, 117), and two in the Nansen Basin (58, 32) with the calculated value (Cal, Eq. 5).

Amundsen Basin (87, 117), and two in the Nansen Basin (58, 32), with the calculated value (Cal, Eq. 5).

3.2.2 Barents Sea

The $t_{1/2}$ in the upper 100 m of the southwestern Barents Sea are longer than those of the central Arctic. However, most remain relatively short compared with the calculated value. (Fig. 4). This region is shallower than the central Arctic and the maximum depth sampled was 300 m. Station 169 has the shortest $t_{1/2}$ values. Station 173 is the closest to the continent, and the $t_{1/2}$ values are longer than those at Station 169. This station is influenced by coastal currents carrying fresher surface waters, which could contain a terrestrial DOM signal originating from mainland Norway. The 173 it is indeed much fresher than the stations 169 (Rabe et al., 2016). The station 149 on the other hand, has also freshening at surface, but most likely then from sea ice melt, so it is probably at the Polar Front, the stations in between 173 and 149 are very “Atlantic”, with high salinity and high temperatures (Rabe et al., 2016). Although, in general $t_{1/2} < t_{1/2cal}$, there are significant variations between stations. Stations 157 and 161 stand out with the longest $t_{1/2}$ at depths of 96 m and deeper than 200 m with $t_{1/2} > t_{1/2cal}$ ($p < 0.05$).

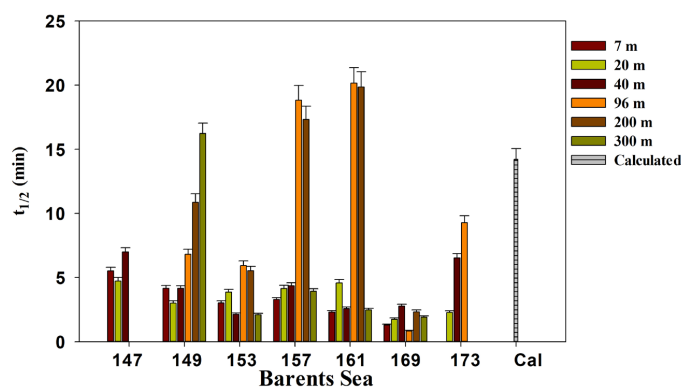


Figure 4. The Fe(II) half-life ($t_{1/2}$) values at all the vertical profile in the stations in the Barents Sea, with the calculated value (Eq. 5).

3.3 Station-based comparison of $t_{1/2}$ and DOM characteristics

When comparing observed $t_{1/2}$ of Fe(II) in the different regions to DOM distribution, it was obvious that the concentration of DOC (Fig. 5A), terrigenous and protein Parafac components (Fig. 5B,C) and lignin phenols (Fig. 5D, E) exhibited similar spatial patterns, with higher values of DOC, lignin phenols and terrigenous fluorescence in the central Arctic Ocean (stations in the Makarov and Amundsen Basin) relative to the Nansen Basin and Barents Sea and higher values in surface waters (<100m) relative to deeper waters (Figure 5A-E). Stations 96 and 101 in the Makarov Basin stand out as having the shortest Fe(II) $t_{1/2}$ (Fig. 3A) and the highest concentrations of DOMt while longer Fe(II) $t_{1/2}$ and lower DOC, lignin phenols and fluorescence concentrations were observed in the Barents Sea stations (Fig 4). This agrees well with the general spatial distribution of terrigenous DOM in Arctic Ocean surface waters recently shown (Amon et al., 2024). The terrigenous humic-like components dominated the fluorescence signal in the central Arctic Ocean with values higher than 0.12 in the OSW for Amundsen and Makarov Basins. The protein-like components displayed values below 0.04 RU, except on station in Makarov Basin which were slightly higher (Fig. 5C).

These results indicate that the Amundsen and Makarov Basins were characterized by elevated DOC concentrations ($>80 \mu\text{mol L}^{-1}$), while Lignin and FDOM analysis showed a predominance of DOMt in the top 100m at these stations.

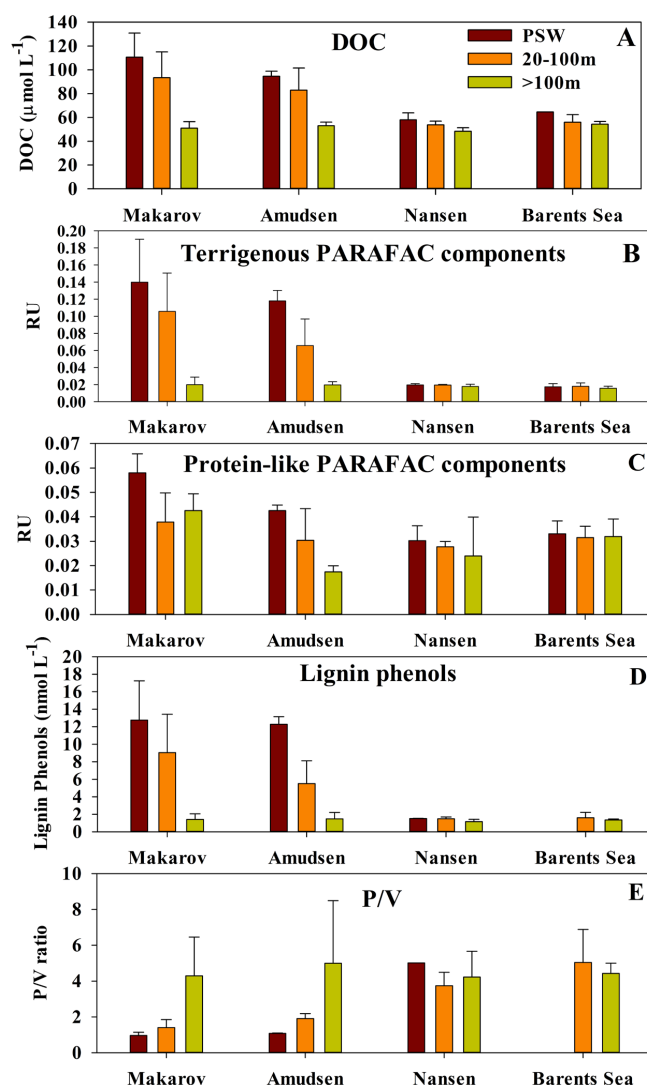


Figure 5. The mean values of (A) DOC and the PARAFAC components: (B) terrigenous humic like components, C₄₉₂ and C₄₅₆, C₄₁₁, C₄₀₄, and (C) protein like components, C₃₃₈ and C₃₀₂, (D) Lignin phenols and (E) P/V are shown for stations in Makarov Basin, Amundsen Basins Nansen Basin and Barents Sea.

The concentration of lignin phenols was $> 10 \text{ nmol L}^{-1}$ in surface waters of Makarov and Amundsen Basins (Williford et al., 2022), 5 to 10 times higher than in Nansen Basin and Barents Sea surface waters as well as deeper waters ($>100\text{m}$). In addition to lignin phenol concentrations, the surface waters of the TPD stations were also characterized by a different lignin fingerprint. Looking at the ratio of p-hydroxyphenols to vanillyl phenols (P/V), TPD surface waters carry lignin with much lower P/V ratios indicative of fresher



DOMt compared to diagenetically altered lignin in deeper waters and surface waters in the Nansen Basin and Barents Sea (dominated by Atlantic water inflow). P/V ratios are reliable indicators of lignin age or diagenetic stage (Amon et al. 2012). The difference in P/V ratios indicates that different water masses have varying qualities of DOMt, the TPD surface waters seem to have relatively fresh DOM coming from the Siberian shelf, while deep waters and surface waters in the Nansen Basin and Barents Sea have low levels of DOMt that has been degraded for a much longer time. However, one has to keep in mind that lignin phenols only contribute <1% to the total DOMt and that most of the DOMt remains chemically uncharacterized, particularly with respect to binding sites for Fe(II) and Fe(III). The presence of DOMt could explain the acceleration of the Fe(II) oxidation resulting in a $t_{1/2}$ shorter than the calculated value, as suggested in previous studies (Lee et al., 2016, 2017a; Santana-Casiano et al., 2022). Strong organic binding ligands have been reported for Amundsen and Makarov Basins related with humic substances of riverine origin (Slagter et al., 2017).

On the other hand, in the Nansen Basin and the Barents Sea the DOC concentration was relatively low ($48\text{--}63\text{ }\mu\text{M L}^{-1}$) and the fluorescence signal of PARAFAC components shifted from a terrigenous dominance to a protein-like dominance with generally lower levels compared to the TPD ($<0.03\text{ nm}^{-1}$). Moreover, the concentration of lignin phenols was $<2\text{ nmol L}^{-1}$, indicating low levels of DOMt (Williford et al., 2022). In these regions, DOM of autochthonous origin likely contributes to the observed decrease in the oxidation rate constant, producing longer $t_{1/2}$ than in the central Arctic Ocean.

4. Discussion

The experiments were conducted at constant pH and temperature under oxygen-saturated conditions, ensuring that the thermodynamic factor remained controlled throughout the study. Likewise, all experiments were performed in the dark, thereby excluding potential photo-oxidation effects. In addition, samples were filtered through $0.2\text{ }\mu\text{m}$ membranes, which also ruled out the influence of particulate components. Once all the aforementioned factors were controlled, it could be assumed that the main factor potentially conditioning this process was the presence of organic matter. In this context, variations in $t_{1/2}$ across basins, stations, and with depth highlight spatial differences in Fe(II) persistence, likely driven by changes in DOM characteristics, including origin and remineralization, associated with the different water masses.

Previous studies in the subarctic area in the Irminger and Labrador seas have suggested that changes in the oxidation rate constants could be related to the effect of organic matter complexing iron and changing the species involved in the mechanistic oxidation process (Santana-González et al., 2018, 2019). The first attempt to correlate observed changes in $t_{1/2}$ with CDOM and FDOM properties was done in coastal waters in the Macaronesia region (Santana-Casiano et al., 2022).

In relation with DOM, in the surface waters of the Arctic Ocean, different geographic regions have been identified based on the distribution of DOC, CDOM/FDOM and lignin (Gonçalves-Araujo et al., 2018; Stedmon et al., 2011; Williford et al., 2022). Although DOC provides information on the amount of DOM in the ocean, it does not provide information on its characteristics. To identify the origin and characteristics of the DOM, the use of the optical properties of CDOM, including Parallel Factor Analysis (PARAFAC)



of FDOM provides a great tool to make a first estimation, even when many individual compounds could contribute to the observed signals (Santana-Casiano et al., 2022; Stedmon et al., 2007). The PARAFAC analysis enabled to distinguish between the terrestrial and marine origin of the organic compounds in the marine environment. In the case of terrestrial material, lignin provides an unequivocal proof for its terrigenous origin (Williford et al., 2021). In this sense, the characterization of the DOM was essential for interpreting the Fe(II) persistence in the ocean. The deviations observed in $t_{1/2}$ when compared with $t_{1/2,cal}$ (k'_{obs} compared with k'_{cal}) may be due to the interaction of Fe(II) with the DOM under controlled physicochemical conditions (pH, T, and S). The variability in the oxidation rate constant ($\Delta k'$) is expressed using Eq. 6. To explain some of the variability, it is necessary to consider, in this context, the origin and characteristics of the DOM found at the stations studied.

4.1 Circulation patterns and waters masses distribution

The distribution of DOM and dissolved iron is affected by circulation patterns of the water masses involved and provides a comprehensive framework to explain Fe(II) behavior. The Makarov and Amundsen Basins, in the central Arctic, are most affected by the path of the TPD that transports DOMt from the Siberian rivers and shelves toward the North Atlantic (Charette et al., 2020). The influence of the TPD is mainly constrained to the upper water column, particularly within the Polar Surface Waters (PSW) and the halocline (approximately the upper 30–120 m), where riverine and terrigenous DOM signatures are most pronounced (Amon et al., 2024; Koenig et al., 2026). The Nansen Basin is dominated by AW characterized by low levels of DOM and is unaffected by the TPD (Arnone et al., 2023; Koenig et al., 2026; Slagter et al., 2017; Williford et al., 2022; Wunsch et al., 2025). The Makarov Basin surface waters can show Pacific water influence entering from the Canada Basin, producing a highly stratified upper layer, while AW governs in the Nansen Basin and then modifies Amundsen Basin with freshwater input from rivers and sea ice melt. In Nansen Basin, the PSW are above (shallower than 150 m) the saltier and warmer AW, but here PSW have no influence from riverine waters (Koenig et al., 2026; Wunsch et al., 2025). In the Nansen and Amundsen Basins, Eurasian Basin Deep Water (EBDW) is found at depth, while in the Makarov Basin the more isolated Canadian Basin Deep Water (CBDW) is present (Rudels, 2012, 2015). While Makarov and Amundsen Basins present a similar behavior in surface waters for $t_{1/2}$, in the deep water the behavior was different. In the Makarov Basin, $t_{1/2}$ for the two stations studied, was close to the $t_{1/2,cal}$ while in the Amundsen Basin $t_{1/2}$ was shorter, with the highest values obtained at a depth of 1000 m. Nansen Basin showed low $t_{1/2}$ values both in surface and at deep waters, with longer $t_{1/2}$ values in the PSW that decreases in Arctic intermediate waters and in the bottom waters.

The Barents Sea receives little input of DOM from major rivers or other terrestrial sources as reflected in the low levels of DOMt (Petit et al., 2022; Rudels, 2012, 2015; Sandven et al., 2023; Slagter et al., 2017). Other studies using FDOM components in the Barents Sea confirm that protein-like FDOM dominated in the surface layer of the Barents Sea (Makarewicz et al., 2018; Petit et al., 2022). Concentrations of marine and terrestrial humic-like FDOM were low and distribution of those components were vertically homogenous in the upper 100 m (Makarewicz et al., 2018). The CDOM absorption properties observed in the Barents Sea (Hancke et al., 2014) were comparable with values found in the North Atlantic Ocean (Kowalczyk et al., 2013), with the CDOM origin of autochthonous characteristics (Hancke et al., 2014;



457 Makarewicz et al., 2018). The predominantly autochthonous nature of the DOM in this area could explain
 458 the different behavior observed in terms of Fe(II) persistence when compared with the central Arctic. In the
 459 Barents Sea, the circulation pattern (Fig. 1) is complex, it is a frontal zone between the Atlantic and polar
 460 waters. AW is transported northward by the North Atlantic Current, with the Barents Sea branch flowing
 461 into the Barents Sea as the Norwegian Current. Meanwhile, polar surface waters (PSW) enter the Barents
 462 Sea via the East Spitsbergen Current, which originates as transformed polar water from the northeastern
 463 Barents Sea (Sternal et al., 2014). Therefore, the DOM they transport may have different origins and
 464 characteristics that affect the kinetics of Fe(II) oxidation potentially including organic matter from melted
 465 sea ice due to the warm Atlantic water.

466

467 4.2 Influence of iron-organic complexation on Fe(II) oxidation kinetics

468 Based on the information obtained in this study, it can be considered that, in the marine environment, Fe(II)
 469 can interact with DOM of autochthonous or allochthonous origin, which can be grouped into pools of
 470 marine (L_m) and terrestrial ligands (L_t).

$$471 L_j = L_m + L_t \quad (8)$$

472 This interaction results in Fe(II) complexes ($\text{Fe(II)}L_j$) that can be oxidized to Fe(III) at different rates (Eq.
 473 9 and 10) or remain as FeL in seawater



476 However, the interaction of Fe(III) with ligands may also influence the persistence of Fe(II) in the medium
 477 through the following reactions



480 If these reactions occur, a decrease in k' is observed, not necessarily because the rate of Fe(II) oxidation
 481 decreases, but because Fe(II) is generated due to the redox reaction between Fe(III) and the ligand (Eq. 11
 482 and 12). L can be involved in abiotic redox processes through its interaction with Fe (Eq.12), or biotic
 483 redox as in many biological processes (Morel and Price, 2003).

484 Previous studies in seawater focusing on individual compounds have demonstrated that organic compounds
 485 can affect the Fe(II) oxidation kinetics, either accelerating or slowing it down. In some cases, they may also
 486 form highly stable complexes with Fe(II), thereby maintaining the metal in solution. Investigations
 487 involving hydroxycarboxylic acids showed that glucaric acid, 1,4-glucarolactone, and citric acid
 488 accelerated k' , whereas glucuronic, glycolic, gluconic, lactic, tartaric, glyceric, and malic acids retarded it
 489 (Kuma et al., 1995). Studies examining the influence of amino acids reported that cysteine enhanced k' ,
 490 likely through complexation reactions with Fe(II), while alanine and glutamic acid exhibited negligible
 491 effects (Santana-Casiano et al., 2000; Theis and Singer, 1974). An increase in k' has also been associated
 492 with a higher proportion of heteroaliphatic carbon (Craig et al., 2009). Furthermore, seawater enrichment
 493 experiments with phytoplankton exudates revealed an increase in k' attributed to elevated concentrations of
 494 dissolved uronic acid (Samperio-Ramos et al., 2017, 2018). The importance of hydrophobic and
 495 allochthonous DOM in accelerating Fe(II) oxidation in freshwater systems has also been demonstrated. In
 496 particular, Fe(II) oxidation rates increased in the presence of humic-type DOM characterized by a high



aliphatic carbon content (Lee et al., 2016, 2017b, a). It is precisely this behaviour that we have observed in this study for the central Arctic Ocean samples. On the other side, the protein-type DOM from phytoplankton and microbial derived DOM (DOMm) tends to decrease the oxidation rates in seawater and for this reason they could explain the longer $t_{1/2}$ observed in the Barents Sea (González et al., 2014; Lee et al., 2017b, a).

Studies of complexation in the marine environment have mostly focused on Fe(III) and conducted in terms of dissolved iron concentration (dFe). The comparison of Fe-organic ligand binding properties (Rijkenberg et al., 2018; Slagter et al., 2017) between stations in the Arctic and the Barents Sea shown significant differences for the same cruise, as with the kinetic studies of Fe(II). In the Arctic, these differences were primarily driven by the riverine influence within the TPD, whereas in the Barents Sea, they were influenced by the effects of the continental shelf, phytoplankton, and Atlantic water content. The Fe-L complex formation constant ($\log K_{FeL}$) values did not differ significantly between basins in the central Arctic, which only indicates that different ligands able to complex dFe have similar affinities (strong or weak ligands) or there is a balance in the different affinities for the detection window used in the determination (Slagter et al., 2017).

Although, most dFe is present as Fe(III) in oxic environments, the amount of dissolved iron is the sum of Fe(II) and Fe(III) species (eq. 13) and complexation reactions between these two species and the ligands may occur.

$$TdFe = dFe(III) + dFe(II) \quad (13)$$

$$TdFe + L_j \leftrightarrow dFe(III)L_j + dFe(II)L_j + dFe(II) + L_j \quad (14)$$

Considering the above, the presence and nature of organic ligands must be taken into account when evaluating the effect of organic matter on iron redox processes, and equation 2 needs to be improved (15).

$$\sum_j k_{L_j} \cdot FeL_j = \sum_m k_{L_m} \cdot FeL_m + \sum_t k_{L_t} \cdot FeL_t \quad (15)$$

DOM interacts extensively with iron through the formation of both Fe(II)-L and Fe(III)-L complexes, consistent with previous observations on the complexation and redox buffering capacity of dissolved organic matter (Daugherty et al., 2017). Carboxyl functional groups associated with aliphatic compounds, as well as humic substances, are key contributors to the redox behavior of natural organic matter because they provide multidentate binding sites for iron complexation (Hay and Myneni, 2007; Krachler and Krachler, 2021; Leenheer et al., 1998). In addition, hydroxyl-bearing moieties, particularly catechol groups present in polyphenols and numerous siderophores, are also important in mediating iron redox transformations (Blazevic et al., 2016). Recent studies using liquid chromatography, high resolution mass spectrometry (LC-FT-ICR-MS) and Nuclear Magnetic Resonance (NMR) have characterized the functionality of natural DOM in terrigenous and marine samples (Cai et al., 2025; Kong et al., 2026; Matos et al., 2025) pointing to the ubiquitous abundance of carboxyl-rich alicyclic molecules (CRAM) and other functionalities potentially serving as ligand binding sites.

332

333 4.3 Environmental controls on residual Fe(II) oxidation kinetics

334 The PLSR was used to explain the relative influence of interrelated environmental variables and to assess
335 their collective role in explaining the variability in the observed oxidation behaviour, $\Delta k'$ (Fig. 6). This



analysis provides a framework for evaluating the extent to which natural environmental conditions modulate Fe(II) oxidation beyond physicochemical conditions. The PLSR model applied to the central Arctic Ocean stations (32 and 58 in Nansen Basin, 96 and 101 in Makarov Basin, and 117 at the border of Nansen and Amundsen Basins) identified a single latent component as optimal according to cross-validation. This component explained 55.2% of the variance in the predictor matrix and 38.0% of the variance in $\Delta k'$. Overall model performance indicated a moderate but significant relationship between the selected environmental variables and residual Fe(II) oxidation variability ($R = 0.617$, $R^2 = 0.380$, $RMSE = 0.772$). Among all predictors, the strongest contributions according to VIP scores were observed for humic-like DOM proxy C456 (VIP = 1.23), dissolved organic carbon (DOC; VIP = 1.21), salinity (VIP = 1.18), nitrate (VIP = 1.11), and silicic acid (VIP = 1.09). Pressure showed moderate importance (VIP = 0.87), whereas protein-like DOM proxy C338 contributed weakly (VIP = 0.67). Phosphate showed negligible predictive relevance (VIP = 0.04). Standardized regression coefficients indicated positive associations between $\Delta k'$ and C456, DOC, and silicic acid, while salinity and nitrate were negatively associated with $\Delta k'$. Pearson correlations supported the PLSR findings. Significant positive correlations with $\Delta k'$ were observed for C456 ($r = 0.56$, $p = 0.003$), DOC ($r = 0.55$, $p = 0.003$), and silicic acid ($r = 0.50$, $p = 0.010$), while salinity ($r = -0.54$, $p = 0.005$) and nitrate ($r = -0.51$, $p = 0.008$) showed significant negative relationships. Because $\Delta k'$ represents the difference between observed and calculated Fe(II) oxidation kinetics, the obtained relationships provide insight into environmental factors not captured by standard abiotic variables.

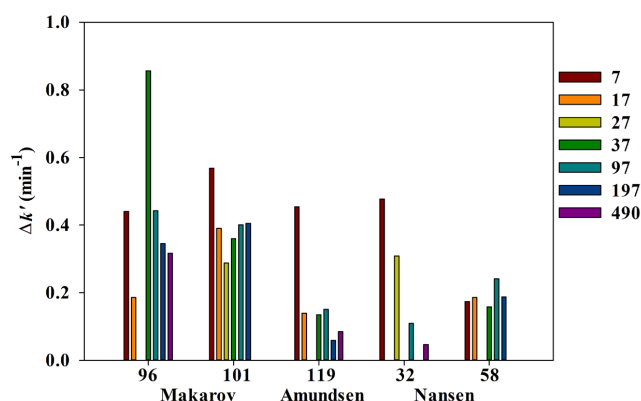


Figure 6. The $\Delta k'$ for stations 96 and 101 (Makarov Basin), 117 (Amundsen basin) and 32 and 58 (Nansen Basin) at different depths.

The strong association between $\Delta k'$ and both DOC and fluorescence-derived DOM signatures suggests that dissolved organic matter plays a significant role in modulating Fe(II) oxidation beyond the effects of pH, temperature, and salinity alone. This is consistent with previous evidence that organic ligands can alter Fe



redox kinetics through complexation, stabilization of intermediate species, or modification of reaction pathways. The positive relationship with the humic-like optical proxy C456 further suggests that DOM composition, rather than simply bulk concentration, may influence the magnitude of these kinetic deviations. Fluorescent DOM components may reflect chemically reactive ligand pools capable of interacting directly with dissolved Fe species. The negative association with salinity may indicate that the processes responsible for enhancing deviations from theoretical oxidation kinetics are more prominent in fresher waters (river water and sea ice melt), potentially reflecting shifts in DOM source, ligand composition, or water mass characteristics. The inverse relationship with nitrate and the positive association with silicic acid suggest that $\Delta k'$ may also be linked to broader biogeochemical gradients, including water mass history, remineralization state, or biologically mediated chemical environments. Importantly, the reduced PLSR identified a single dominant latent component, indicating that the unexplained variability in Fe(II) oxidation kinetics is primarily structured along one coherent environmental gradient rather than multiple independent mechanisms. However, the moderate explanatory power of the model ($R^2 = 0.38$) indicates that a substantial proportion of $\Delta k'$ variability remains unresolved, suggesting that additional controls such as uncharacterized ligand chemistry, reactive oxygen intermediates, microbial processes, or methodological uncertainty may also contribute. It is important to note that FDOM measurements do not capture the entire DOM pool, as they represent only the fluorescent fraction of DOM. Similarly, CDOM measurements characterize the optically active, light-absorbing fraction of DOM, whereas a substantial portion of DOM is neither fluorescent nor optically detectable.

584

585 Conclusions

In the central Arctic Ocean the presence of allochthonous DOM derived from riverine and terrestrial inputs can significantly modify the redox potential of the Fe(II)/Fe(III) system, thereby influencing Fe(II) oxidation kinetics. Terrestrially sourced DOMt is typically rich in humic and fulvic substances containing carboxylic, phenolic, and quinone functional groups that strongly complex Fe species and alter their thermodynamic stability. These complexes can promote electron-transfer reactions through redox-active moieties acting as electron shuttles. In addition, DOM can inhibit iron precipitation and maintain iron in dissolved or colloidal forms, extending Fe residence times in Arctic waters.

In contrast, the Barents Sea exhibits DOM with a more pronounced autochthonous origin. In this region, DOMm is predominantly derived from phytoplankton and microbial production, resulting in a higher contribution of protein-like compounds. Autochthonous, protein-type DOM has been associated with decreased Fe(II) oxidation rates in seawater, likely due to the formation of organic complexes that stabilize reduced Fe species and modify electron-transfer processes.

The k' ($t_{1/2}$) obtained for the Fe(II) oxidation kinetics therefore reflect the net effect of organic compounds that either accelerate or retard the oxidation process. Consequently, Fe(II) oxidation kinetics depend on the balance between DOM components that promote oxidation and those that stabilize reduced iron species. In general, allochthonous DOM enriched in lignin-derived and humic substances appears to enhance Fe(II) oxidation, as observed in regions influenced by terrestrial and riverine inputs, whereas autochthonous DOM



603 derived from marine biological activity tends to reduce oxidation rates by stabilizing dissolved Fe(II)
604 species and/or through the reduction of Fe(III)-L complexes.
605 These findings suggest that the origin and composition of DOM play a critical role in regulating Fe redox
606 dynamics, with distinct biogeochemical implications for Arctic shelf systems influenced by marine
607 production compared to those dominated by terrestrial inputs.

608

609 **AUTHOR INFORMATION**

610 **Author Contributions**

611 J.M.S-C and D. G-S designed, coordinated, and wrote the initial draft.
612 J.M.S-C, D. G-S, A.G.G, and M.G-D performed the tasks related to Fe kinetics studies. R.M.W.A., M.A.G.,
613 H.E.R, and T.W performed the tasks related to DOM analysis and interpretation. M.A.G. supervised the
614 section on physical oceanography, including Fig. 1. All authors contributed to the manuscript writing and
615 editing.

616

617 **Competing interest**

618 The authors declare no competing financial interest.

619

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626

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