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Interactive comment on "Sources of Fe-binding organic ligands in surface waters of the western Antarctic Peninsula" *by* Indah Ardiningsih et al.

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We thank the referee for these kind words, the thoughtful comments and efforts towards improving our manuscript.

Major comments

1) I do not completely agree with the use of the reference Seyitmuhammedov 2020, being a PhD thesis not available. If it had been used just for a minor aspect, it would have been ok, but it is often cited, particularly for data that are present there but not presented in this manuscript. First of all, I think some additional detail for the DFe analysis (section 2.2) could be useful and I suggest to add them. However, the main problem is related to the values of labile particulate Fe and Mn (section 4.1), δ18O and

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dissolved and total-dissolvable Fe (section 4.2). In order to help readers, I think that they could be presented at least with ranges. Maybe it could have been smoother to publish those values before submitting this manuscript, to have a proper reference to cite.

Reply: We have added additional detail for DFe analysis in section 2.2 (lines 135 - 149):

“The DFe analysis is described in detail by Seyitmuhammedov et al. (in review). In short, the DFe analysis was conducted using highâĂŘresolution inductively coupled plasma mass spectrometry (HR-ICP-MS) using a Thermo Fisher Element XR instrument at NIOZ, the Netherlands and using an Amtek Nu Attom instrument at the University of Otago, New Zealand. Samples were UV-oxidized and pre-concentrated using an automated seaFAST system (SCâĂŘ4 DX seaFAST pico; ESI) equipped with Nobias-PA1 chelate resin. The quantification was done via standard additions. The recovery of the resin was ∼100% and was verified in every analytical run by comparison between the slope of the seawater calibration curve and the eluent acid calibration curve after (Biller et al., 2012). Accuracy and reproducibility were monitored by regular measurements of the reference materials SAFe D1 and GEOTRACES South Pacific (GSP) seawater, and an in-house reference seawater sample, North Atlantic Deep Water (NADW). Results for DFe analyses of reference samples were 0.722 ± 0.008 nM (n = 3; NIOZ) and 0.729 ± 0.018 nM (n = 6; U. Otago) for SAFe D1 2013 (consensus value = 0.69 ± 0.04 nM) and 0.155 ± 0.045 nM (n = 13) for GSP 2019 consensus values. The average overall method blank (seaFAST and ICP-MS), determined by repeatedly measuring acidified ultrapure water in every analytical run as a sample, was 0.05 ± 0.02 nM (n = 21).”

The ratio of labile particulate Fe and Mn in the open ocean was 0.27 ± 0.49, and has been added in the text (line 326).

“Additionally, the ratios of labile particulate Fe to labile particulate Mn (0.27 ± 0.49;

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Seyitmuhammedov et al. (in review) indicate that Fe has a biogenic origin in the off-shore waters (Twining et al., 2004)." the range of the δ18O results from oxygen isotope analysis was added in lines 373 – 375. "the results of oxygen isotope (18O/16O, conventionally reported into delta-notation as δ18O; Seyitmuhammedov et al. (in review) analysis showed δ18O values ranged from -0.56 – 0.06 ‰Ṫhese values were used to with estimated fractions of sea-ice meltwater (-1.9 – 1.1 %) and meteoric meltwater (precipitation and glacial;0.3 – 3.9 %)."

The range of DFe and total-dissolvable Fe in the study region during the sampling period was added in lines 386 – 387):

"the conditions along the WAP were not homogenous and elevated Fe (ranged from 0.08 – 4.88 nM for DFe and 0.16-85.42 nM for total-dissolvable; (Seyitmuhammedov, in review)) concentrations northeast of our transect were observed in the upper 100 m, suggesting that some of the observed ligands might have been transported south-westerly with the CC."

The values of labile particulate Fe and Mn (section 4.1), δ18O and dissolved and total-dissolvable Fe will be available separately upon publication of Seyitmuhammedov et al. (in review). Similarly, the more detail procedure of DFe analysis will be available in Seyitmuhammedov et al. (in review).

2) I looked at the dataset presented in the reported link (https://doi.org/10.25850/nioz/7b.b.5) and I have some questions or remarks with the presented data and their use in the Results or Discussion sections.

2a. Fluorescence. What do negative values for fluorescence mean? Are they just a consequence of improper calibration or do they have another meaning? In addition, there are some fluorescence data missing (two depths for Station 70 and all the depths for Station 72), hence I wonder how the plots were drawn for Figure 5b. Please clarify.

Reply: Fluorescence data is obtained from a sensor attached to CTD rosette. The

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negative values only occur in the deeper than 100m where normally phytoplankton concentrations are really low. The calibration equation that is used to convert Volts to chl-a concentration in units of 'mg/m3' apparently creates negative values for the concentration when there is basically no chl-a. Thus, the negative values are basically 0 mg/m3. In our data, the lowest negative value is > -0.018, which is close to zero. The maximum fluorescence in the CTD file is about 2.43, and 0.018 is only a small percentage of the max. Finally, we have added the missing data and added the explanation above in the caption of figure 5 and 'read me' text of table.

2b. DFe. Are data for St 90 40 e 100 m below the LOD? I ask that because that there is no standard deviation for those parameters, and also because the standard deviation of the blanks is reported as 0.02 nM (line 134), hence the LOD should be around 0.06 nM by using the 3σ method, which is higher than the values reported for those two samples (0.05 nM). If so, I think it should be clearly expressed, but in that case I wonder how the values could be plotted in Figure 3b (maybe as half the LOD?) and how the CLE-AdSV analyses were performed for those two samples, since they would need a value of DFe for the voltammetric titration. Please clarify this aspect and make the corrections if needed.

Reply: Yes, DFe at St90 at depth 40 and 100 was below the LOD and these samples are presented as the value of the LOD without an error. This is stated at the end of the paragraph 215. The LOD is 0.05 calculated from 3xSD of the blank (blank SD = 0.016 ; LOD is 0.054). However, we reported in 2 significant figures hence 0.05 instead of 0.06 nmol/L. We used the DFe concentration of 0.05 nM for these two samples.

2c. Silicate. Why data for Silicate are not reported in the table? Also, in line 314, to express the purpose of the Si* values, the authors comment that "a negative Si* indicates Fe limiting conditions", but in their dataset there are no negative values for Si*. Please explain better this point

Reply: we have added Silicate data to the table. Based on the cited literature, a nega-

tive value of Si* indicates Fe limiting conditions. In our dataset, there were no negative values for Si*, however, some values were close to 0 (e.g at the open ocean station). Our data indicates that although there is no Fe-limitation yet during our sampling period, Fe limitation could potentially occur later in the season. We have added the explanation above in the lines 326 – 330, as copied below:

"The lowest concentrations of DFe (<0.05 nM) were observed at St. D and E and were a result of both biological uptake and limited supply. This area most likely represent Fe-limited conditions as indicated by declining Si* (Si*= [Si] – [N]) values and high ratios of [nitrate]/DFe (Figures 6a and 6b). The value of Si* serves as a proxy for Fe limitation, where Fe stress leads to preferential drawdown of Si compared to N by diatoms in surface water (Takeda, 1998). A negative Si* indicates Fe limiting conditions, assuming that Si and N are required in a 1:1 ratio by diatoms (Brzezinski et al., 2002). In our dataset, although there were no negative values for Si*, some Si* values at the open ocean stations were close to 0. Our data indicates that although there is no Fe-limitation yet during our sampling period, Fe limitation could potentially occur later in the season."

Minor comments

- Line 38: correct CO2 ("2" in subscript). Reply:done

- Section 2.1: please define the material of the 0.2 μm filters used for filtration and the volume of the GO-FLO bottle. Although the conservation procedures are correct, I wonder why the samples for Fe-binding ligands and DFe were collected separately, instead of freezing just one bottle and take the aliquots for the two analyses from the same "container" in the lab (of course acidifying before DFe analysis). Reply: we have added the information on the material of the filters and added the volume of GO-FLO bottle (lines 117 - 120).

"Seawater samples for DFe and Fe-binding ligands in this study were obtained using 12 L GO-FLO bottles attached to a Kevlar® wire. Seawater samples were filtered over

0.2 μm filters (cellulose acetate, Sartroban 300, Sartorius®) into pre-cleaned sample bottles inside a trace metal clean van." DFe samples were acidified immediately on-board to minimize the adsorption to the bottle wall. Previous Based on previous studies (i.e Jensen et al. (2020)) and based on our experiences, the DFe concentration from the ligand sample bottles are somewhat lower than the DFe concentration from immediately acidified samples due to precipitation in unacidified samples.

- Figure 1: I suggest using a darker yellow to indicate the Coastal Current. Reply: done.

- Section 2.2: please report the certified or informative values of SAFe D1 and GSP samples. In addition, report also the LOD of the procedure. Reply: we have included the certified values of SAFe D1 and GSP samples (lines 140 - 141). Also, the LOD of the procedure is added (lines 141 - 142).

- Line 153: in "CLE-CSV" there is an "Ad" missing before "CSV". Reply: Done.

- Line 156: the full stop at the end of the sentence is missing. Repy: done.

- Line 158: please close the parenthesis which was opened before "αFeÎDL". Reply: done.

- Line 160: the authors refer to αFeL, but I guess they meant αFeÎDL instead? ËĞ Reply: corrected.

- Figure 2: please uniform the indication of "c." for the third figure, using the two parentheses consistently with (a) and (b). Also, in the caption, the "θ" in "$\sigma\theta$" should be in subscript. Finally, Absolute Salinity is reported with "A" in subscript or as plain SA in the text and in the Figures, please uniform in the whole manuscript. Reply: done.

- Line 189: I think there is some problem with the "" for Absolute Salinity. Did the authors mean "33.0 < SA < 33.7"? Reply: corrected.

- Figure 3: there is a reference missing (and an unclosed parenthesis) in "DFe, data

from;". Also, what do the author mean when they say "with colors denoting depth the values of [Lt]"? I guess there's a "depth" in excess? Reply: corrected.

- Line 233: please remove the comma after [L']. Reply: done.

- Figure 5: why in some images the profiles are "smooth" (e.g. b) and in others are "rounded" (e.g. a and c)? Also, in Figure 5a there are only the profiles for the 5 stations, well separated, while for example in Figure 5c there are more. Why? Reply: Fe-binding ligand samples are only taken from 5 stations, therefore, in Figure 5a, where [L'] is presented, there are only the profiles from the 5 stations. For nutrient analyses (in this case, nitrate), samples were taken in a few more stations than ligand samples. Similarly, for Fluorescence data, this data is obtained from the sensor attached to CTD rosette, and fluorescence is recorded whenever the CTD is deployed to obtain seawater for many different analyses, thus we have higher resolution data for fluorescence.

- Line 264: I think the "that" is in excess? Reply: corrected.

- Line 284: since it is one value, it should be "maximum", while "maxima" is used for plurals (accordingly, correct also line 298 from "maximum" to "maxima" if it is referred to more than one). Reply: done.

- Line 298: unclosed parenthesis in "(St. 84 and 90; (Figure 5b)". Reply : done

- Figure 6: please insert the unit of measurement for Si*. Moreover, in the Figure there is "[Nitrate]/[DFe]" while in the caption there is "[Nitrate]/DFe", please uniform (DFe is presented without parentheses in the whole manuscript). Reply: done

- Line 325: please revise the "which commonly produced by" part, I do not think the sentence is fluid. Reply: the sentence is revised into two sentences.

- Line 367: "a phytoplankton blooms": it should be either "a phytoplankton bloom" or "phytoplankton blooms", please correct. Reply: corrected

- References are not well uniform in the use of the doi. Maybe there are also some parts

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missing (e.g. pages or article number for Arrigo 2008, Lam 2011, Lannuzel 2016, etc.).
Reply: we have checked the references and use the DOI uniformly in each reference. We also checked the journal volume and pages for all the references.

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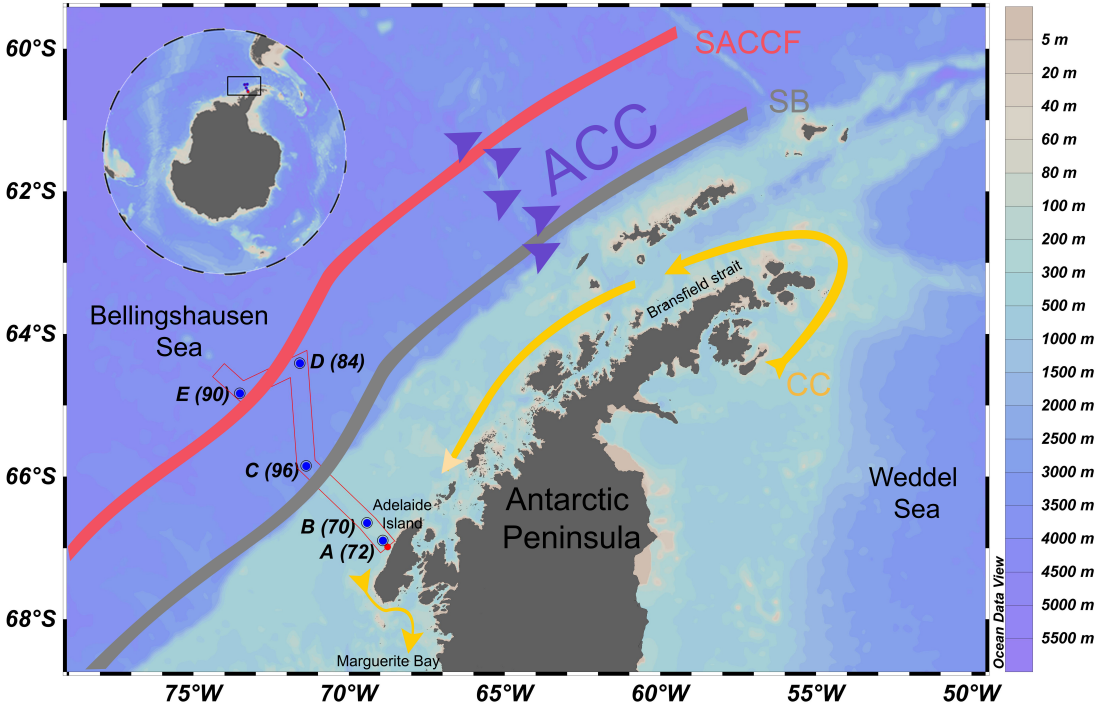

Fig. 1. Map of the sampling sites along our study transect near the Western Antarctic Peninsula.

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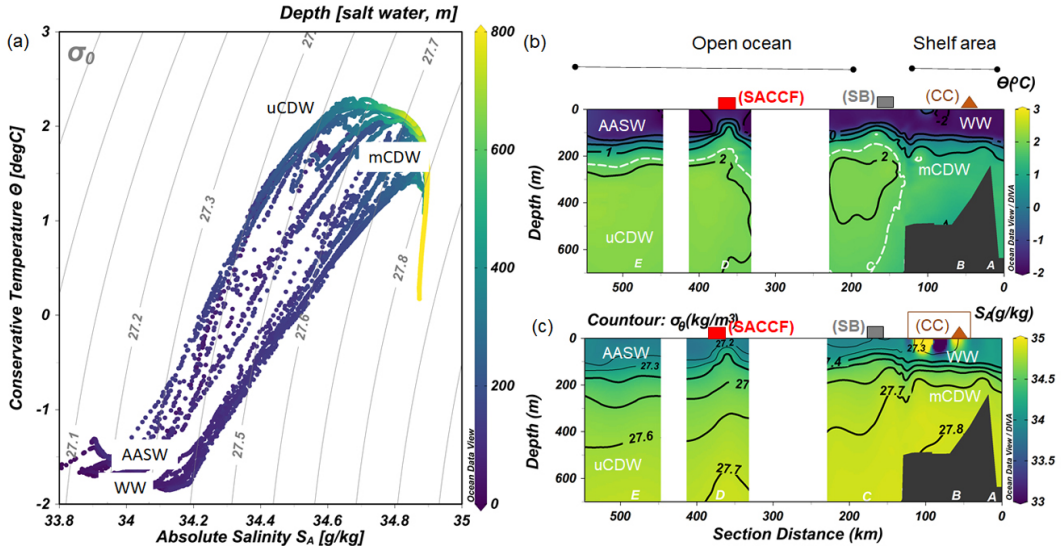

Fig. 2. (a) Diagram of absolute salinity (SA) versus conservative temperature (Æ§) with isopycnal lines and colors denoting depth in m. The distribution along the transect shown in Figure 1 of (b) Æ§ and (c) SA

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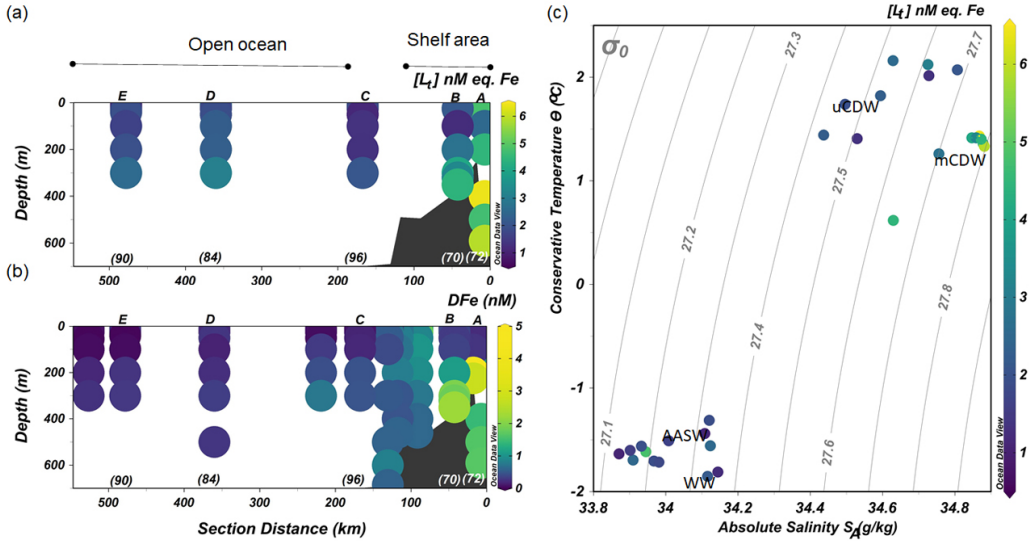

Fig. 3. The distribution along the transect shown in Figure 1 of (a) the concentrations of total Fe-binding ligand [Lt] and (b) concentrations of dissolved-Fe (DFe);and (c) a Æ§- SA diagram

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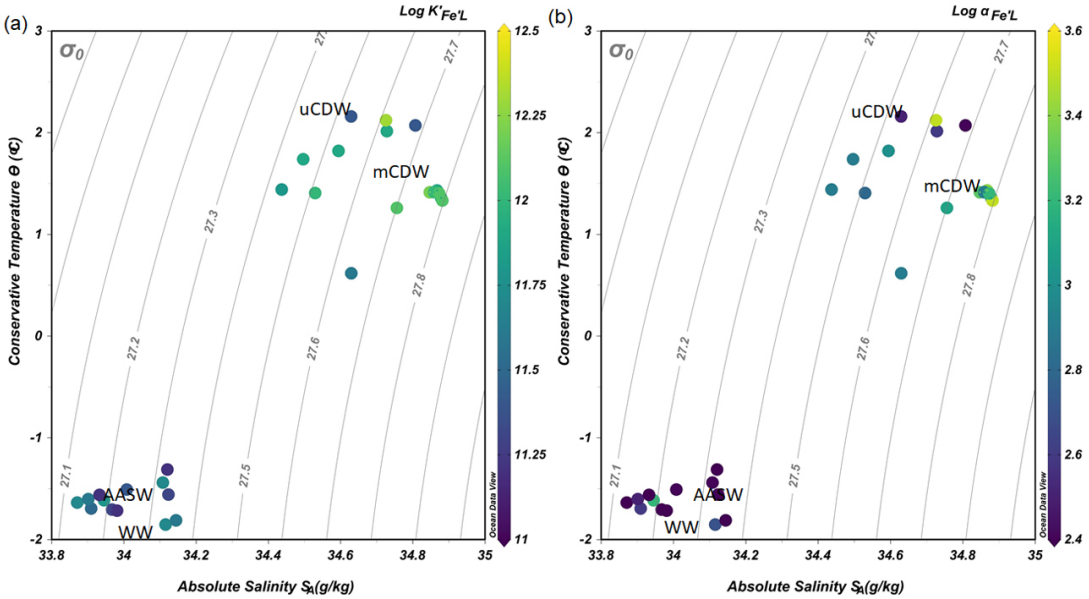

Fig. 4. (a) The binding strength, log "K" _"Fe'L" ^"cond" and (b) complexation capacity, log αFeÎĎL plotted in a Æ§-SA diagram. The color scale indicates the values of log K and log αFeÎĎL.

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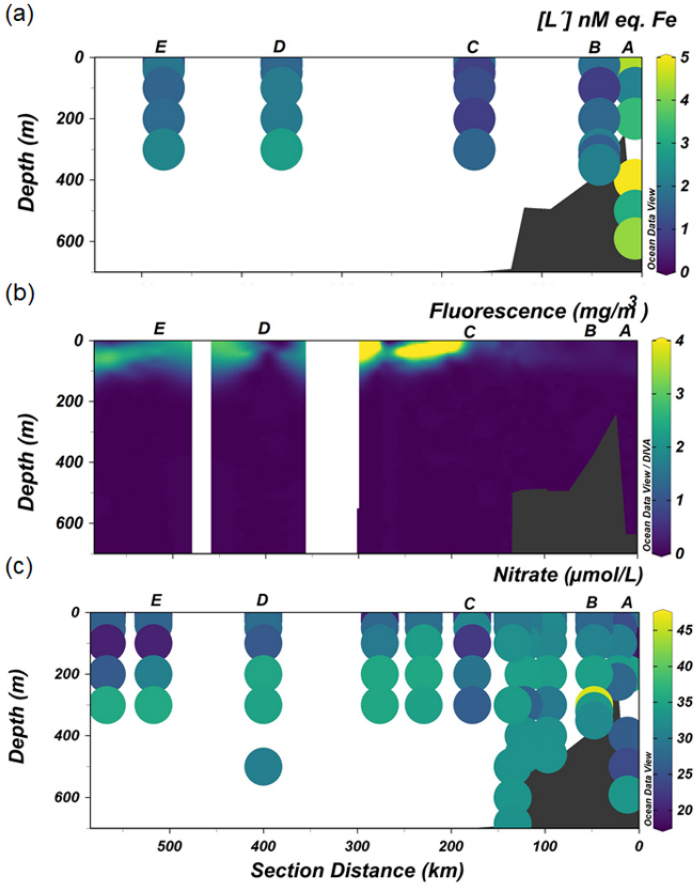

Fig. 5. The distribution along the transect shown in Figure 1 of (a) excess ligand concentrations [LĬD], (b) Fluorescence, and (c) Nitrate.

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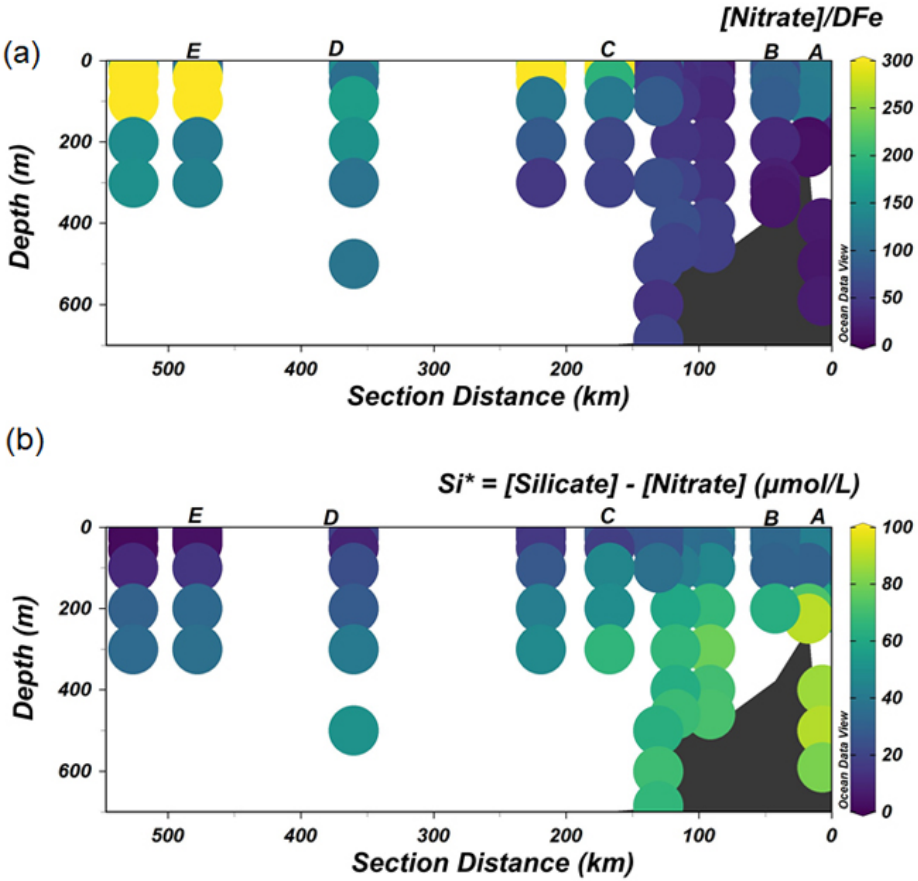

Fig. 6. The distribution of Si*(a) and the ratio of [Nitrate]/DFe (b) along the transect shown in Figure 1.

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