Responses to reviewers (R:) (Marked-up text R1 compared to R0 below).

Meso and micro-cosms were sampled at different locations. The explanation of these experiments is very hard to follow. I am not sure all information is necessary, at least in the main manuscript. A simple table like table 1B is in my view enough.

R: This is obviously a matter on which there are different opinions between different co-authors and different reviewers with some wanting more detail and some wanting less. As a companion text describes the same set of mesocosms (which will be linked on the BGS website), we have reduced the method section further again but are reluctant to remove much more material.

From all these experiments FeII was measured and some samples were taken to observe FeII oxidation rates in the dark. In the end the explanation of different results hardly needs the differences between the experiments, the more reason to move text on the "cosms" to the supplementary information.

R: Yes the 'chemists' working on this project would certainly agree with this opinion, but others would argue that the exact setup with respect to light availability, filtering of the water, adding of zooplankton etc are all important details which may have unintended effects on Fe biogeochemistry and thus feel that it is important to include them.

The authors missed one important publication Rijkenberg et al., 2006. In this paper the influence of organic ligands of FeIII and FeII on photo-reduction and oxidation of Fe are studied. In the present text it is assumed to be important, I agree, and the Rijkenberg publication can certainly help here instead of referring to papers where speculation on this subject can be found.

R: We had missed the relevance of the Fe(II)-PPIX work in this paper because the manuscript primary concerns Fe(II) formation rates from Fe(III)-L species, but the comment on Fe(II) production in the dark at the end of the text are indeed useful and compliment the comments from Reviewer 2 concerning the possibility of 'dark' Fe(II) production from a superoxide driven redox cycle. An additional paragraph is added in the discussion under the topic of 'dark' Fe(II) production: "*Apart from the influence of organic Fe(II) ligands on Fe(II) stability arising from the slower oxidation rates of some complexed Fe(II) species, Fe(II) binding organics may also have a role in the generation of superoxide which is speculated to be a dominant mechanism for the formation of Fe(II) in the dark. Experiments with 65-130 nM of protoporphyrin IX demonstrate increased formation of Fe(II) in the dark with both increasing porphyrin concentration and increasing irradiation of seawater prior to the onset of darkness (Rijkenberg et al., 2006). Whilst the rates of this process are challenging to investigate at the sub-nanomolar porphyrin concentrations expected in natural seawater, the dark formation of Fe(II) mediated by ROS interactions with Fe(II)-organic complexes could potentially be important in both the diurnal cycling of Fe in the surface ocean and the non-photochemical formation of Fe(II) in the dark of the ocean's interior (Rose 2012). From a mechanistic perspective, it is difficult to establish from the experiments here in whether apparent Fe(II) stability arises from reduced oxidation rates due to Fe(II) complexation, or dark Fe(II) formation via a mechanism, such as that proposed for superoxide, which involves Fe(II)-organic complexes."*

One of the reasons that the text is hard to follow is the use of different names for the same

locations/experiments (there are 5 locations: the Arctic (Svalbard), the Mediterranean (probably Crete), Patagonia, Gran Canaria and Kiel (mentioned only once and not in methods, but important for the discussion)). Since the setup is so complicated it is even advisable to mention experiments in the same sequence (helping the reader) and not as in the example given changing the sequence in one sentence: "MesoArc than for MesoPat (MesoPat R2 0.0022, gradient 0.0049 ± 0.014; MesoArc R." etc The introduction tells the reader that she/he can expect mesocosm experiments in three places. Then section 2.1 starts and experiments were done in 4 places en in the result section experiments in Kiel appear to have happened too. Extra names like the ocean Certain project come out of the blue. First meso is used later without any explanation on page 14 Meso Med, MicroPat MultiPat are used. These last set meso micro and multi are much better suited because they indeed indicate which kind of experiments are meant. Why not use them immediately and define them properly?

R: In hindsight this in confusing to the reader. The reason was we had used the exact terminology adopted by the projects that ran the mesocosms, but this can be confusing as 'MesoPat' was used [within the project that funded it] to refer to the field campaign (which included a mesocosm/multistressor/microcosm in Patagonia). We have therefore adopted a standardized name for each specific experiment e.g. 'MesoPat' refers to the mesocosm in Patagonia, 'MicroPat' refers to the microcosm in Patagonia etc… and adopted these throughout the text.

Section 3.5 is very interesting but difficult to read and understand. Half of the text should be in methods, also be more clear about the Kiel experiments (at least I suspect the spiked Atlantic tests are done in Kiel).

R: As suggested (here and later), we have moved any descriptive material including equations to the method section. Yes the 'Kiel' experiments are those with Atlantic seawater, we now refer only to 'spiked Atlantic seawater experiments'

And it is not clear whether the different treatments had influence on the results.

*****R: This is a key point of the paper which we try to clarify better. We can't address this question (whether the different treatments had influence on the results) because the 'stability' of Fe(II) measured is very sensitive to the Fe(II) concentration at the time the experiment starts (i.e. the time at which seawater is moved into the dark). This is the fundamental finding of the paper (and is raised in some other points below, so I will address it extensively here). Conceptually, in simple terms, there are two Fe(II) 'pools' in seawater when it sits under ambient surface conditions – whether in a mesocosm, or not.**

- **A) There is a pool of inorganic Fe(II) which has oxidation rates exactly as predicted by experiments where Fe(II) is spiked into synthetic seawater.**
- **B) There is a pool of organic Fe(II) associated with natural organic material akin to ligands which, overall, has a slower oxidation rate than the inorganic pool.**

Therefore, when a seawater sample is sub-sampled for analysis and moved to the dark (in a bottle, or in opaque tubing flowing into a flow injection analyzer), Pool A decays faster than Pool B. The fraction of the total Fe(II) present as B therefore increases in the seconds-minutes after sample collection.

Hence a major sampling problem; even if seawater is pumped straight into a flow injection analyzer using the best available method (a duel-loop FIA system), it experiences 30-60 seconds in the dark prior to analysis. In reality this time is 2-4 minutes due to the time required for subsampling, moving FIA lines, achieving stability with the luminol signal etc… During this time the fraction of Fe(II) present as Pool B increases. And because the half-life of pool A is short, the fractional importance of (B) can increase significantly within minutes of being in the dark.

As (B) is potentially capped by something akin to 'ligand saturation', whereas (A) in time periods of minutes-hours is limited mainly by the rate of photochemical formation, the relative size of B compared to A is also likely to change on diurnal timescales due to the diurnal cycling of Fe(II).

Therefore, there is a strong bias towards measuring oxidation rates close to the calculated inorganic rates at times of day when there is a large total Fe(II) pool, and when the decay rate is measured from the exact time at which a sample is moved into the dark. Conversely, there is a strong bias towards measuring apparent Fe(II) stability when the decay rate is measured at a time of day when the total Fe(II) pool is smaller, and when the decay rate is measured from some time after a sample has been moved into the dark.

Unfortunately, with any sort of field experiment it's very difficult to measure more than 1 or 2 decay rate experiments simultaneously, so the time of day when an experiment was conducted varies within each experiment set, and it's impossible to produce an experimental setup free from artefacts where the sample time/'move to dark time' is completely identical to the time at which the first sample peak is measured. There is inevitably a delay and unfortunately the delay, even if varying only from 30-60 seconds, can be equivalent to 1-2 Fe(II) half-lives for inorganic Fe(II) species.

For these reasons it is not meaningful to look at the difference between treatments within or between mesocosm experiments for the Fe(II) decay rate because the decay rate is biased by the initial Fe(II) concentration for the decay rate experiment and this cannot easily be corrected for.

In the discussion I miss apart from the Rijkenberg paper, discussing the influence of the different sampling and measurement treatments and the different experimental conditions.
Is the difference in time between sampling and analysis discussed, Gran Canaria is different from the others. Can this have had an effect on the results? See also above section 3.5. What is e-microcosm (in Suppl table),this is not explained, still here the largest differences between kmeas and kcal exist.

R: A line is explicitly added to discuss the potential effect of sample acidification. We provide a reference (as in the original text) which describes this in detail. We did not conduct kinetic experiments in Gran Canaria, therefore there is no direct potential for this method -change to affect our main conclusions… *"a modification outlined by Hansard and Landing (2009) which is not thought to significantly affect in-situ Fe(II) concentrations during the short time period between collection and analysis".* **We also note that in warm seawater there is simply no alternative as the half-life of Fe(II) limits the ability to do any analysis on unamended seawater. 'E-microcosm' was the official project name for the 'MicroPat' experiment (hence comment above, the official project 'names' are difficult to follow, so we have**

standardized and amended throughout). Yes this experiment shows the highest Δk. But, as noted above (*R) it is very challenging to claim this due a specific biogeochemical phenomena.**

Detailed comments Sections 2.1 and 2.2 are hard to follow
Sentences like "Note that previously a series of experiments in the Mediterranean ('MesoMed') was also included." do not help. If it was previously, why do we bother here.

R: As raised by another reviewer, it is important to note that we attempted these measurements but do not present data (because every single measurement attempted was below detection) to avoid miss-reporting of our findings.

Line 7-9 page3 section 2.1 seem out of place, this has nothing to do with setup and sampling.

R: Moved to results section

Line 13: 10 identical 1000-1500L tanks, 5 tanks got zooplankton. According to table 1A they all received copopods but the addition was different per location.

R: No, table 1A simply lists the variables which were manipulated in each experiment. Table 1B gives the specific treatment for the high zooplankton tanks. We clarify in table B that the treatment is the zooplankton added to the 'high grazing tanks' and not the baseline for all tanks (which was zero, the tanks were filtered through a mesh, and then zooplankton were re-added to 'high' tanks only).

I did not find figure S1, below text and pictures, there is a caption but no schematic figure of the experimental design.

R: There is a table for each experiment matrix. Figure S1 is re-labelled 'Supplementary material' rather than a 'Figure'

Line 26: can bags stand? Are bags mesocosms?
In the next line the word tank is used, is this still the same thing?

R: One of the mesocosm experiments used bags (Gran Canaria), two of the experiments used tanks (MesoPat/MesoArc). 'mesocosm' is used widely within the field to refer both to mesocosm experiments (i.e. the whole experiment), but also to each unit within a mesocosm experiment, hence why we try not to use both meanings in the same sentence. We have rephrased throughout now using only the term 'mesocosm experiment' to refer to a whole experiment.

Section 2.2 What is a 10-treatment?

R: an experiment with 10-treatments.

Section 2.3,line 26 after cleaning, what happened with the bottles? Were they stored empty or filled, if so with what.

R: They were stored 'empty' (or full of air). Now stated explicitly.

Page 7: were the FeII bottles dark plastic?

R: No, to move Fe(II) samples from the experiments to the FIA (which took 1-2 minutes), we opted form transparent containers so the water would remain exposed to ambient light. It was then transferred into a dark box as stated in the

text at a time recorded as 'time zero'. We rephrase and clarify this sentence. In Gran Canaria, where the Fe(II) samples were acidified, the bottles were opaque to prevent any further photoproduction of Fe(II).

Line 9: Ocean certain is? It would be so much easier when the normally used names are used here too, meso/micro-Med-Arc-Pat.

R: We now use the terms Meso/micro/multi-Med/Arc/Pat throughout.

Section 2.5: What happened in Kiel? Line 18 tells us what happened in Patagonia and Svalbard (? Pat and ARC, Comau fjord-Kongsfjorden?)

R: we now explicitly add the names (meso/micro-Med-Arc-Pat) when referring to any fieldsite and refer to the laboratory spiked experiments consistently as spiked seawater experiments.

In 3.5 79 experiments are mentioned, that info belongs here. How many per location. Were they kept under ambient temperature, where is the laminar flowhood

R: Details added to the methods section. All of these experiments were in temperature controlled rooms with temperatures as per the collected water for analysis. Page 8 s2.5 re-written accordingly, … 'All Fe(II) decay experiments were conducted inside the temperate controlled rooms hosting the MultiPat/MultiArc experiments. As such, a constant temperature was maintained throughout these experiments. The FIA instrumentation was arranged with the inflow lines under a laminar flow hood inside the temperature controlled rooms….'

3.1 why use the name Svalbard here and not MesoArc.

R: Ammended.

Page 10 line 11, no glucose is mentioned in Table 1

R: No, this was only in the text, now amended.

Page 11 line 9: curiously..Why.is this curious, and why give relations that are not relations, for figures 2 and 4. For figure 4 it is not clear which line belongs to which mesocosm experiment. No idea what the journal guide lines are, but especially as in figure 3the './ 'is confusing like there is a ratio instead of the unit.

R: Because we can't think of a simple reason why there should be a strong correlation between DFe and TdFe in one mesocosm, but no correlation at all in another, especially when the strongest correlation is for a low organic carbon, high particulate Fe site. Figures 2 and 4 are removed to save space. Units are changes on the graphs throughout.

Page 13 line 1 as per?

R: There are obviously multiple manuscripts in preparation from this series of meso/multi/micro experiments. One concerns H2O2 (in BGS, the manuscripts will be linked as companion papers so the link will be more obvious).

Page 14: Meso Med, MicroPat MultiPat: have mercy on your reader! Suddenly new abbreviations. However, useful abbreviations that should be used throughout the whole manuscript

R: We have now adopted our own standardized terms for the experiments as per previous comments.

Lines 9-10: Is that to be expected? Reference needed here (also at line 16)

R: Yes, this is discussed in the next paragraph (in the original text). A Reference is added.

9-16, a lot of different names for the same sites

R: Yes, but each mesocosm obviously has a corresponding fieldsite so we inevitably have to name the experiment and the site. For clarity we annotate the place names with the experiments hosted at that location.

29: chlorophyll a Italic Figures 5 are too small. Lables and legend are impossible to read and the sequence in the legend is not logic, one legend might be enough for 5a and 5b. Perhaps make 5 c a separate figure. Be careful with ratio's. The high values are they due to low DFe? Figure 5 c is not mentioned in the text.

R: Amended so the figures display better whilst merged in the text. The legend sequence order is changed. C is shown separately and we now show the concentrations and the ratio (DFe is never particularly low, so no these are not an artefact of sub-nanomolar DFe concentrations).

Line26: I do not know whether there is a general decline as claimed here, the 1450 microatm perhaps does decreases but the 1300, 700 and 1150 microatm do not, so no general decline here. This figure is not suited to make such statements. An increase between days 20-29 ok.

R: The significance of changes (other than the increase after day 20) is variable between treatments, as this doesn't really affect our conclusions we slim the text accordingly and remove these lines.

Page 15: line 6: what is number 7?

R: Changed to PCO2 value for this mesocosm.

Lines 6-9: not clear what the authors tell here? Is this still about figure 5b? The sixth mentioned number does not show an increase, not the seventh. They have different CO2, haven't they?

R: We clarified this 'number' (above) referred to a specific treatment. It is the 6th number because one mesocosm leaked and was removed from the experiment (this is all clarified by just referring to the treatments by PCO2 target level throughout rather than arbitrary treatment labels).

Page 16, Line 11: which variation, give reference, do not force the reader to search in another of your papers to find out.

R: The specific variations compared were a dual-loop configuration as described by Croot and Laan (2002) and a pre-concentration method as described by Bowie et al., (2002)

Lines12-14: it depends what you mean with in situ and what you want to do with the k-values. With such an uncertainty one can wonder whether waiting for stabilisation would have been wiser.

R: But then any Fe(II) present would have decayed and we would have to conducted spiked experiments, which wouldn't tell us much about stabilization that we didn't already know. This error is not large considering comparable data in the literature considering what reported 'errors' actually include. Note the exact opposite query is raised by reviewers with Sarthou et al., (2011) BGS. In this excellent 2011 manuscript the authors added small Fe(II) spikes to seawater in order to determine oxidation rates and it was questioned (see comments/discussion with reviewer 2 on that text) whether this approach was meaningful compared to observing in-situ decay rates. Hence our rationale for the setup herein.

Lines 20 onwards: is this what happened in Kiel? Most of this belongs to the method section. Also the equations belong to the method section in my view.

R: Yes, we have moved equations and experiment descriptions to the methods section.

Page 17:I can add a few hypotheses: the aged Atlantic water was probably filtered, in any case no phytoplankton or copepods were present. The added Fe for certain saturated the organic ligands and thus this DFe was in an inorganic form, a colloidal or amorphous Fe-oxide or hydroxide. This is where the equations 2 and 3 were made for: inorganic Fe! So certainly this is other chemistry. I advise to read Rijkenberg et al., 2006 Geochimica et Cosmochimica Acta 70 (2006) 2790–2805; Enhancement and inhibition of iron photoreduction by individual ligands in open ocean seawater.

R: Yes, these experiments represent inorganic speciation and this is exactly what we summarize in hypothesis III. Note the experiments concerning ligand saturation in the Rijkenberg 2006 text concern Fe(II) formation from Fe(III) species, a slightly different issue to the Fe(II) decay discussed here.

Page 18:line one, why would low FeII be the most stable?

R: See * comment above; because the fraction of this Fe(II) existing in a stable form is likely higher.**

Discussion line 18: This can be read that TFe behaves conservatively. Why would DFe-TFe be linear, that is a strange idea. That is assuming all particles have the same properties.

R: In these near-shore waters where a large fraction of Fe comes from a near-point source (e.g. the freshwater outflow into the Pat/Arc fjord sites) it is not an unreasonable statement that all particles have the same properties, note the relative consistency in XRF data, simply because freshwater derived particles account for the vast majority of Fe-rich particles in the water column. On short timescales TdFe does behave conservatively, unlike the rapid removal of DFe in these nearshore environments, a TdFe/S plot is linear showing that the sinking/modification of TdFe takes longer than the residence time of water in these fieldsites.

Page 19: table 4 why is mesopat meso and multistressor so different, this is not discussed. Why is the sequence different, why Svalbard whereas it is Arctic. The different names makes it more difficult to understand.

R: Noting the large standard deviation on both Fe(II)/DFe and DFe/TdFe, it is not clear that they are 'so different'. We clarify that the 'ambient' measurements are at the fieldsite. But as the 'ambient' measurements don't refer to any of the experiments at that fieldsite, they need a separate name. For clarity we sate 'Arctic (Svalbard)'.

Lines 23-24: why was this not mentioned in the method section?

R: The exact timing of the experiments is shown in the data table appended to the paper and thus we don't feel it necessary to write it out in the methods section. The aim of these experiments was to investigate how Fe(II) decayed, not to produce high resolution Fe(II) time-series across the duration of every mesocosm.

Page 20 line 8-9: thus what is the conclusion?

R: **A line is added,** 'The ambient concentrations of Fe(II) measured in Patagonia (Comau fjord) and the Arctic (Svalbard, Kongsfjorden) at the mesocosm experiment fieldsites are therefore not necessarily directly comparable to Fe(II) concentrations measured after nutrient addition in the mesocosm experiments.'

4.3: line 16: according to the methods section artificial light was used in micro and multistressor but not in Mesocosm, so why mention artificial light here?

R: The text states 'due to the enclosed HDPE mesocosm design and/or synthetic lighting'**. The point being made was that all of the mesocosm/microcosm/multistressor experiments where Fe(II) decay experiments were conducted had low H2O2 concentrations.**

Lines 21-25: read Rijkenberg, they saw the influence of ligands on Fe redox, of ligands binding Fe III en of a ligand binding FeII. That should be added in the discussion here.

R: Photochemical formation of Fe(II) from Fe(III)-L species is not relevant to the discussion here. The specific points concerning dark Fe(II) formation from porphyrin are added at the end of this section as per some earlier comments.

Page 21decay rates in the e-microcosm are different from the calculated k compared to the others, apart from low FeII at t=0? (low Fe(II) occurs also in other experiments) what is e-microcosm, what is different? Could that be an extra reason. Use the work of Rijkenberg et al in the discussion on page 21, they did not assume FeII ligands, they used one in their redox rate experiments.

R: (E-microcosm is the data label for the MicroPat experiment, we have changed this in the text to 'MicroPat' as per our standardized names). There is no obvious experimental difference between the MesoPat/MicroPat/MultiPat experiments that immediately provides an easy explanation for why the largest changes in K should be reported for datapoints from one experiment. There may of course be species-level effects due to the different biological communities at the start of, and throughout, each experiment. Yet, as we note (R*), because the discrepancy between measured and calculated K is very sensitive to the Fe(II) concentration at t=0, and because it is not (using the design here) possible to rigorously standardize t=0 so that [Fe(II)] at t=0 is constant, or to account for the change in Fe(II) concentration and speciation between in-situ conditions and t=0, it is very difficult to deduce any relationships between biogeochemical parameters and the difference in K.**

Excel file temp in k, make capital, add start or initial also to the column name for FeII. The precision does not warrant the decimals shown with 35% uncertainty. What is an e-microcosm, why are the rates so high here. Add measured to k. No Kiel experiments here?

R: Amended. (See above comment also). 'Kiel' (spiked Fe(II) decay experiments) data is now added to the supplementary file as per the Meso/Micro/Multi data.

This manuscript addresses a topic that is relevant to the scope of Biogeosciences. There is a clear rationale for the work, the experiments have been carefully designed and executed, and the data analysis and interpretation are reasonable. However, I felt that the scope of the paper needs to be more accurately represented and that some details relating to the experiments and data analysis were missing. Overall, I believe that this manuscript should be published after revision. SPECIFIC COMMENTS 1. The title of the manuscript is too broad, to the extent that I find it misleading. The manuscript does not directly address the issue of Fe(II) stability in seawater – there are no measurements of thermodynamic constants (which the word "stability" implies), nor measurements or calculations of complex speciation, the underlying mechanisms are inferred or hypothesised rather than explicitly measured or tested, and the measurements are limited primarily to coastal seawater. This is all perfectly valid, but the manuscript really addresses iron redox speciation in coastal mesocosm experiments, and I would prefer to see a title more along these lines.

R: New title suggested: "Fe(II) stability in coastal seawater during experiments in Patagonia, Svalbard and Gran Canaria." We accept that, to a chemist, 'stability' would imply thermodynamic stability, but in an environmental context -and considering how the term is used in prior Fe(II) work- it is challenging to find an alternative phrase within a limited title word count.

2. The assertions about "over-use of the "99%" statistic" (i.e. that "99% of DFe in the oceans is hypothesized to be present as Fe(III)-complexes" are subjective and I find this aspect of the Introduction to be overstated. It is true that "this observation explicitly or implicitly underpins the formulation of DFe in global marine biogeochemical models", and that the influence of Fe redox speciation is often ignored. The authors also provide a nice summary of compelling evidence that Fe(II) is important in "two specific environments". However, it does not automatically follow that the assumption that 99% of DFe is present as Fe(III)-complexes is invalid everywhere in the oceans, or that the "99% statistic" is "over-used". To make this assertion objectively would require something like a meta-analysis of the literature to quantify the number of papers that make this claim, and the proportion of those that make this claim incorrectly. In my opinion, it would be better to just present the evidence and let the reader decide if they think this is an "over-used" statistic. I would suggest that the authors review the Introduction to remove or tone down subjective statements and ensure that any assertions are supported by an appropriate number of references.

R: Agreed, as the text is already quite long we have no desire to extent it further with an unnecessary literature review. Given that the key point is that all global biogeochemical models represent dissolved Fe basically as a dissolved Fe(III)-L species without the complication of a redox cycle, we delete the line in question, *['Yet, as evidenced by over-use of the "99%" statistic, the presence of a fraction of DFe as Fe(II) in surface waters –exactly where most primary production occurs- is widely overlooked.]'* And, as per other comments, this is replaced with a brief over-view of Fe(II) measurements in the deep ocean. '*Fe(II) concentrations at depth are less well characterized, although there is extensive evidence of pM Fe(II) concentrations occurring throughout the pelagic water column suggesting that 'dark' Fe(II) production is a widespread phenomenon (Sarthou et al., 2011, Sedwick et al., 2014, Schallenberg et al., 2015).*'

3. In the Introduction there is a strong focus on why Fe(II) is important, but the background about what is known in relation to the abundance and behaviour of Fe(II) in the ocean seems incomplete. For example, the growing body of work (including by some of the co-authors of this manuscript) around the influence of organic exudates from marine phytoplankton on Fe(II) oxidation kinetics is not mentioned in the Introduction, but this would seem critical to understanding much of the manuscript and its rationale. In addition, while there is a brief overview of Fe(II) dynamics in the photic zone and in suboxic zones, it would also be useful to briefly review reports of Fe(II) measurements in other parts of the ocean.

R: An extensive discussion of the role of organics on Fe(II) 'stability' is included in the discussion (as per the original text'.

We now also include a few lines of introduction to this subject in the introduction. 'Fe(II) speciation in seawater and the

potential role of ligands in Fe(II) biogeochemistry is however still uncertain. Organic Fe(II) ligands, akin to Fe(III) ligands in seawater but likely with different binding constant ranges and functional groups (Boukhalfa and Crumbliss 2002), are widely speculated to affect the oxidation rate of Fe(II) in seawater (Santana-Casiano et al., 2000, Rose and Waite 2003, Gonzalez et al 2014). Yet characterizing the concentration and properties of organic Fe(II) ligands in natural waters using titration approaches, as successfully adapted to determine Fe(III)-speciation, has proven challenging (Statham et al., 2012) due to practical difficulties in stabilizing Fe(II) concentrations without unduly affecting its speciation. Never-the-less a broad range of cellular exudates have been demonstrated to positively affect Fe(II) concentrations in seawater, either via enhancing Fe(II) formation rates or retarding its oxidation rate (Rijkenberg et al., 2006., Santana-Casiano et al., 2014, Lee et al., 2017).'

4. Analysis of Fe(II) data was based on an assumption of pseudo-first order kinetics, but there are no details on whether this assumption was tested or verified.

R: This is indeed assumed here as elsewhere in manuscripts on the same topic, but also demonstrated to be a reasonable assumption with the linearity of the ln[Fe(II)] vs time response for each spiked experiment where data is presented (these values are already included in the datasheet). This is clarified in the main text …. 'correlation coefficients are noted for each linear regression'….

5. I think it is highly problematic to exclude discussion of the Mesomed Fe(II) results from the manuscript because "Fe(II) concentrations were universally < 0.2 nM" (p. 3, lines 8-9). Given that you are arguing that Fe(II) is widespread and overlooked, excluding presentation of results from one set of mesocosms because Fe(II) was not measurable in those conditions could be perceived as cherry picking data. Again, I think this would be less of an issue if the scope of the manuscript as suggested by the title and Introduction was revised. If this is recast to make it clear that this is a study of Fe(II) dynamics in a discrete set of mesocosm experiments, then I think it is fine to mention the Mesomed experiments in this way without a detailed presentation of results. However, I think it is also important not to overlook these results in the discussion when generalising about Fe(II) behaviour.

R: 0.2 nM was the detection limit. So it isn't the case that we excluded results, not a single [Fe(II)] for any of the Med experiments was above the detection limit of 0.2 nM. This may simply reflect the high temperature of the Med experiments (20°C) and similarly unfavorable pH/Salinity for Fe(II) measurements; the half-life of Fe(II) under in-situ Med conditions was sufficiently short that it would be practically impossible to measure in situ Fe(II) concentrations with a dual-loop FIA system as multiple Fe(II) half-lives occur as sample water is flowing into the FIA. There isn't therefore any insight to be gained from the Med work. The text is changed slightly to address this 'Fe(II) concentrations were universally below detection <0.2 nM….'

6. The discussion about processes contributing to Fe(II) formation lacks mention of superoxide-mediated Fe reduction or other biological ferrireductase processes. This would seem remiss given that recent publications have suggested extracellular superoxide production may well be ubiquitous(e.g. Diazetal., 2013, Widespread production of extracellular superoxide by heterotrophic bacteria, Science 340: 1223-1226) and is likely to influence Fe speciation (e.g. Rose, 2012, The influence of extracellular superoxide on iron redox chemistry and bioavailability to aquatic microorganisms, Frontiers in Microbiology 3:124).

R: As noted, we do not we do specifically investigate the mechanism of apparent Fe(II) stability, but the potential role of O_2^- is certainly of interest in light of the Rijkenberg 2006 work highlighted by another reviewer. A paragraph addressing

this point of interest is added at the end of the discussion. A ubiquitous 'background' production of radicals in the deep ocean by bacteria would indeed be interesting as a potential driver of trace element redox chemistry, but we note it is incredibly challenging to make reliable measurements of trace species under dark pelagic (i.e. below the photic zone) conditions and thus very speculative to comment on the potential significance of O2-/Fe cycling on a grand scale; *'Apart from the influence of organic Fe(II) ligands on Fe(II) stability arising from the slower oxidation rates of some organically complexed Fe(II) species, Fe(II) binding organics may also have a role in the generation of superoxide (O_2^-) which is speculated to be a dominant mechanism for the formation of Fe(II) in the dark. Experiments with 65-130 nM of protoporphyrin IX demonstrated increased formation of Fe(II) in the dark with both increasing porphyrin concentration and increasing irradiation of seawater prior to the onset of darkness (Rijkenberg et al., 2006). Whilst the rates of this process are challenging to investigate at the sub-nanomolar porphyrin and Fe(II) concentrations expected in the ocean's dark interior, the dark formation of Fe(II) mediated by ROS interactions with Fe(II)-organic complexes could potentially be important in both the diurnal cycling of Fe in the surface ocean and the non-photochemical formation of Fe(II) in the dark of the ocean's interior (Rose 2012). From a mechanistic perspective, it is difficult to establish from the experiments here in whether apparent Fe(II) stability arises from reduced oxidation rates due to Fe(II) complexation, or dark Fe(II) formation via a mechanism, such as that proposed for superoxide, which involves Fe(II)-organic complexes.'*

7. The organisation of different aspects of the manuscript needs to be reviewed to ensure material is presented in the correct location. For example, the first paragraph of section 3.1 is discussion, not results. The second paragraph of section 3.1 is methods, not results.

R: Text shifted accordingly. A greater number of subtitles are now used to separate the method/results/discussion of each component.

Details about measurement of hydrogen peroxide concentrations are n provided in the methods section at all, but rather addressed only by the statement "as per Hopwood, 2018" in the results section.

R: A text mainly concerning H2O2 in the mesocosms is also under review for BGS, the two are linked as companion manuscripts and thus we did not want to include unnecessary detail in this already long manuscript.

8. P. 1, line 14. I suggest changing "exclusively" to "almost exclusively" or "primarily". It is not strictly correct to say that dissolved Fe speciation is assumed to consist exclusively of Fe(III)-L, as Fe' is generally also considered (although minor).

R: 'Almost exclusively' used where applicable.

9. P. 2, lines 31-32. The argument that "the potentially widespread presence of Fe(II)" implies that "redox cycling is an important feature of marine Fe biogeochemistry" is a circular argument. The three cited papers do not show that Fe(II) is potentially widespread – they show that Fe(II) is persistent in certain specific environments and locations studied in this papers. I don't mean to be overly critical about this – I think Fe(II) is important and possibly overlooked – but I think it's important to be objective and precise.

R: Rephrased ….'raise interest in the role of redox cycling in the marine biogeochemical Fe cycle.'

10. P. 17, lines 9-11 and 19-21. This hypothesis is not plausible, in my opinion. A difference in rate constants between different Fe(II) concentrations could be related to a difference in chemical mechanism, but should be completely independent of calibration. Also, there are several studies of Fe(II) oxidation kinetics in seawater that have been conducted at low nanomolar concentrations such that there is a coherent mechanistic understanding (and ability to predict) Fe(II) rate constants from the low nanomolar range right through to the micromolar range.

R: Yes there are multiple studies providing excellent formulas for the calculation of the rate constant with varying T/S/pH/O2. Constructing spreadsheets from different formulations does produce small changes in the calculated value of K (or t1/2) which are systematic. These are however minor. Here we opted to use a single, already published, formulation to determine K and we agree that under these conditions (T/pH/O2)-which are generally well covered by experimental rate constant data,- there is low uncertainty in the value of K. But we thought it was important to raise, and eliminate the suggestion nevertheless.

TECHNICAL CORRECTIONS 11. P. 1, line 20. I suggest changing "retarded relative to" to "less than". Rates can be fast or slow, but rate constants are large or small.

R: changed.

12. P. 1, line 25. Please add a qualification to this sentence explaining under what conditions your work challenges these assumptions (e.g. in coastal surface waters?).

R: 'in coastal seawater' added.

13. P. 2, line 8. Ligands are not necessarily small or organic. Perhaps could change this to "Organic ligands (L) capable of complexing Fe(III) can..."

R: 'organic' is added to the prior sentence to clarify. We define ligands as 'small' and 'organic' when referring to filtered DFe in seawater . The supporting references demonstrate that these ligands are organic.

14. P. 2, lines 24-26. 14. This sentence seems like it belongs in the next paragraph... I can't see how this relates to the presence of Fe(II) in suboxic or photic zones.

R: lines now separated.

15. P. 2, line 28. "There is a paucity of Fe(II) data..." – what sort of Fe(II) data?

R: amended 'pelagic Fe(II) concentration'

16. P. 2, line 29. What do you mean by "kinetic availability"? Do you mean kinetic lability?

R: Yes, but specifically in the context of cellular uptake. The kinetic lability of Fe(II) makes its uptake (theoretically) less energetically costly than Fe(III) uptake. (We now use 'lability' to avoid ambiguity). But this is an over-simplistic argument because cellular-uptake systems may be specifically designed to bind Fe(III) at the cell surface, an argument we don't wish to raise here, hence we simply use the Sunda reference to state that it is theoretically more favorable for a cell to uptake Fe(II) than Fe(III) from a simple energetic perspective.

17. P. 2, lines 34-35. “as evidenced by over-use of the 99% statistic” – what evidence? No citations are provided and this is not tested robustly, as stated in point 2 above.

R: Re-phrased to refer exclusively to the use for a formulation based on this assumption in global biogeochemical models (as above).

18. P. 3, lines 6-10. Following on from point 5 above, I find it confusing that some Mesomedresultsareincludedintheresults, butnodetailsareprovidedinthemethods about these experiments, other than these couple of sentences. I think you need to treat this dataset in a similar way to the other mesososm results, namely describe the method details in full, and fully account for the Mesomed results in your discussion.

R: Rephrased for clarity, there are no results, all data was below detection due to the challenge of measuring Fe(II) using the setup herein under warm conditions due to the shorter half-life of Fe(II).

19. Tables 1A and 1B. It would make more sense to me to label these Table 1 and Table 2, as they show quite separate information. Furthermore, it would be useful to provide coordinates for the mesocosm locations in Table 1.

R: Done. Now provided.

20. P. 6, line 4. Can you provide any information about the spectral quality of the lighting?

R: We can provide the exact manufacturer’s description which includes the wavelength distribution of the lamps.

21. P. 6, line 25. Should this be “trace metal clean low density polyethylene” rather than “trace metal low density polyethylene”? 22. P. 7, line 22. Change “as described by (Paulino et al., 2013)” to “as described by Paulino et al. (2013)”.

R: Yes, amended.

23. P. 9, equation 1. Please define precisely the meaning of Vaddition and Vmesocosm.

R: Moved into methods and defined.

24. P. 11, lines 6-7. The sentence “Before presenting...” is redundant and could be removed – this is self-evident to the reader.

R: Removed.

25. P. 11, lines 10-11. Where the correlations statistically significant?

R: For one experiment yes, for the other no. [Section removed following earlier comments]

26. P. 12. Please define the meaning of the error bars on Figure 3.

R: Error bars defined (always standard deviation of 3 measurements).

27. P. 13, line 1. Does “highest resolution” refer to temporal resolution? Please clarify.

R: Clarified, yes, “highest temporal resolution over the experiment duration”.

28. P. 13, lines 14-16. Is linear regression meaningful for these data? Why use linear regression in this case?

R: This section didn’t add much value to the text and following comments from both reviewers the figure and corresponding paragraph are removed.

29. P. 14, lines 2-5. What do the +/- symbols represent here?

R: Standard deviations (now explicitly stated when used and when referring to mean +/- SD for a dataset, n is specified in the text).

30. P. 14, line 4. Change “measurements was” to “measurements were”.

R: Amended.

31. P. 14, line 21. There is no section 3.3. 32. P. 15. Figure 5 is unreadable as it is too small. 33. P. 15, line 11. Should this refer to Fig. 5(c) rather than Fig. 5(b)?

R: Re-structured so the figure is clearer when displayed in word.

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Fe(II) stability in coastal seawater during experiments in Patagonia, Svalbard and Gran Canaria.

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Abstract

The speciation of dissolved iron (DFe) in the ocean is widely assumed to consist almost exclusively of Fe(III)-ligand complexes. Yet in most aqueous environments a poorly defined fraction of DFe also exists as Fe(II~~).~~), the speciation of which is uncertain. Here we deploy flow injection analysis to measure in-situ Fe(II) concentrations during a series of mesocosm/microcosm/multistressor experiments in coastal environments in addition to the decay rate of this Fe(II) when moved into the dark. During 5 mesocosm/microcosm/multistressor experiments in Svalbard and Patagonia, where dissolved (0.2 µm) Fe and Fe(II) were quantified simultaneously, Fe(II) constituted 24-65% of DFe suggesting that Fe(II) was a large fraction of the DFe pool. When this Fe(II) was allowed to decay in the dark, the vast majority of measured oxidation rate constants were ~~retarded relative to~~less than calculated constants derived from ambient temperature, salinity, pH and dissolved O_2. The oxidation rates of Fe(II) spikes added to Atlantic seawater more closely matched calculated rate constants. The difference between observed and theoretical decay rates in Svalbard and Patagonia was most pronounced at Fe(II) concentrations <2 nM ~~and attributed to a stabilising~~suggesting that the effect ~~of cellular exudates upon~~arose from organic Fe(II~~).~~) ligands. This ~~enhanced~~apparent enhancement of Fe(II) stability ~~of Fe(II)~~ under post-bloom conditions, and the existence of such a high fraction of DFe as Fe(II), challenges the assumption that DFe speciation in coastal seawater is dominated by ligand bound-Fe(III) species.

1. Introduction

The micronutrient iron (Fe) limits marine primary production across much of the surface ocean (Kolber et al., 1994; Martin et al., 1990; Martin and Fitzwater, 1988). Fe is required for the synthesis of the photosynthetic apparatus of autotrophs (Geider and Laroche, 1994), is an essential element in the enzyme nitrogenase required for N_2 fixation (Moore et al., 2009), and is important for phosphorous (P) acquisition from dissolved organic P compounds as part of the enzyme alkaline phosphatase (Mahaffey et al., 2014). Fe is thus one of the key environmental control factors~~, or 'drivers',~~ that concurrently regulate marine microbial community structure and productivity (Boyd et al., 2010; Tagliabue et al., 2017). The distribution of dissolved Fe (DFe) in the ocean (Tagliabue et al., 2017; Schlitzer et al., 2018) and the magnitude of the dominant atmospheric (Mahowald et al., 2005; Conway and John, 2014), hydrothermal (Tagliabue et al., 2010; Resing et al., 2015) and shelf sources (Elrod et al., 2004; Severmann et al., 2010) are now moderately well constrained. Furthermore, dissolved Fe(III) speciation has also been explored in depth and it is evident that organic Fe(III)-binding ligands are a major control on the concentration and distribution of DFe in the ocean ~~(Van Den Berg, 1995; Gledhill and Buck, 2012; Hunter and Boyd, 2007). Ligands (L), small organic molecules~~(Van Den Berg, 1995; Hunter and Boyd, 2007; Gledhill and Buck, 2012). Small organic ligands (L) capable of complexing Fe(III), can maintain DFe concentrations of up to ~1-2 nM in oxic seawater which is an order of magnitude greater than the inorganic solubility of Fe(III) under saline, oxic conditions (Liu and Millero, 1999, 2002). Characterising these ligands in terms of their concentrations and affinity for Fe(III) was therefore a major objective for chemical oceanographers over the past two decades using a variety of related titration techniques (Gledhill and Van Den Berg, 1994; Rue and Bruland, 1995; Hawkes et al., 2013). 99% of DFe in the ocean is hypothesized to be present as Fe(III)-L complexes (Gledhill and Buck, 2012) and this observation explicitly or implicitly underpins the formulation of DFe in global marine biogeochemical models ~~(Tagliabue et al., 2016)~~(Tagliabue et al., 2016).

There are however two specific environments in which this widely quoted "99%" statistic is incorrect. The first is oxygen minimum zones, where low O_2 concentrations extend the half-life of Fe(II) with respect to oxidation and thus permit high nanomolar concentrations of Fe(II) to accumulate in the water column accounting for up to 100% of DFe (Landing and Bruland, 1987; Lohan and Bruland, 2008; Chever et al., 2015). ~~The second is surface waters where photochemical processes initiate the redox cycling of DFe and permit measurable (>0.2 nM) concentrations of dissolved Fe(II) to exist in spite of rapid oxidation rates.~~The second is surface waters where photochemical processes initiate the redox cycling of DFe and permit measurable (>0.2 nM) concentrations of dissolved Fe(II) to exist in spite of rapid oxidation rates (Barbeau, 2006; Croot et al., 2008). Fe(II) is reported to account for 20% of surface DFe concentrations in the Baltic (Breitbarth et al., 2009), 12-14% in the Pacific (Hansard et al., 2009), and 5-65% in the South Atlantic and Southern Ocean ~~(Bowie et al., 2002; Sarthou et al., 2011)~~(Bowie et al., 2002a; Sarthou et al., 2011). A significant fraction of DFe is therefore likely present globally as Fe(II) in oxic surface waters. ~~Yet oceanographic sampling of surface waters using rosettes is a poorly suited~~

~~method for the analysis of Fe(II) concentrations where the half-life of Fe(II) is significantly less than the inevitable time delay between sample collection and analysis (Hansard et al., 2009).~~

~~There is thus a paucity of Fe(II) data in the literature due to the formidable logistical challenges in collecting and analysing this transient species at sea~~Fe(II) concentrations at depth are less well-characterised, although there is some evidence of pM Fe(II) concentrations occurring throughout the pelagic water column suggesting that 'dark' Fe(II) production is also a widespread phenomenon ~~(Hansard et al., 2009; Sarthou et al., 2011). The kinetic availability~~(Hansard et al., 2009; Sarthou et al., 2011; Sedwick et al., 2015). The kinetic lability of dissolved Fe(II) relative to dissolved Fe(III) (Sunda et al., 2001), the positive effect of redox cycling maintaining DFe in solution in bioavailable forms- irrespective of whether Fe(II) itself is bioavailable- (Croot et al., 2001; Emmenegger et al., 2001), and the potentially widespread presence of Fe(II) as a high fraction of DFe in surface waters (O'Sullivan et al., 1991; Hansard et al., 2009; Sarthou et al., 2011) ~~imply that redox cycling is an important feature of marine Fe biogeochemistry. Yet, as evidenced by over use of the "99%" statistic, the presence of a fraction of DFe as Fe(II) in surface waters - exactly where most primary production occurs - is widely overlooked. Here, in order to characterize the behaviour of Fe(II) in surface waters we adapted flow injection apparatus to measure in situ Fe(II) concentrations both in a series of mesocosm experiments (Gran Canaria, Patagonia, Svalbard) and in adjacent ambient waters covering a diverse range of physical and chemical properties.~~raise interest in the role of Fe(II) in the marine biogeochemical Fe cycle.

Fe(II) speciation in seawater and the potential role of ligands in Fe(II) biogeochemistry is however still uncertain. Organic Fe(II) ligands, akin to Fe(III) ligands in seawater- but likely with different functional groups and binding constants (Boukhalfa and Crumbliss, 2002), are widely speculated to affect the oxidation rate of Fe(II) in seawater (Santana-Casiano et al., 2000; Rose and Waite, 2003; González et al., 2014). Yet characterising the concentration and properties of organic Fe(II) ligands in natural waters using titration approaches, as successfully adapted to determine Fe(III)-speciation (Gledhill and Buck, 2012), has proven challenging (Statham et al., 2012) due to practical difficulties in stabilizing Fe(II) concentrations without unduly affecting Fe(II) speciation. Never-the-less a broad range of cellular exudates have been demonstrated to affect Fe(II) concentrations in seawater, both via enhancing Fe(II) formation rates and retarding the Fe(II) oxidation rate (Rijkenberg et al., 2006; González et al., 2014; Lee et al., 2017). Here, in order to characterize the behaviour of Fe(II) in surface waters we adapted flow injection apparatus to measure in situ Fe(II) concentrations both in a series of mesocosm experiments (Gran Canaria, Patagonia, Svalbard) and in adjacent ambient waters covering a diverse range of physical and chemical properties.

2.1 Mesocosm set up and sampling (MesoPat/MesoArc/Gran Canaria)

The setup for the same series of incubation experiments from which we discuss results here (Table 1) is reported in detail in a companion paper ~~(Hopwood et al., 2018b). However, for ease of access, a shorter version is reproduced here. Note that~~

~~previously a series of experiments in the Mediterranean ('MesoMed') was also included. During the Mediterranean experiments the rapid oxidation rate of Fe(II) precluded the determination of Fe(II) concentrations. Fe(II) concentrations were universally <0.2 nM and thus no Fe(II) results from the MesoMed experiments are presented herein.~~

~~Briefly, all experiments~~(Hopwood et al., 2018a). However, for ease of access, a shorter version is reproduced here. Briefly, all experiments (Table 1) used coastal seawater which was either pumped from small boats deployed offshore, or from the end of a floating jetty. Two of the outdoor mesocosm experiments (MesoPat and MesoArc) were conducted using the same basic design in different locations. For these mesocosms, 10 identical 1000-1500 L tanks (high density polyethylene, HDPE) were filled ~95% full with coastal seawater passed through nylon mesh to remove mesozooplankton. Fresh zooplankton (copepods) were collected at ~30 m by horizontal tows with a mesh net, stored overnight in 100 L containers and non-viable copepods removed by siphoning prior to making zooplankton additions to the mesocosm tanks. After filling the mesocosms, the freshly collected zooplankton were added to 5 of the tanks to create contrasting high/low grazing conditions~~.~~ (Table 2). Macronutrients (NO_3/NH_4, PO_4 and Si) were added daily. Across both the 5-high and 5-low grazing tank treatments, a ~~DOC~~dissolved organic carbon (DOC) gradient was created by addition of glucose to provide carbon at 0, 0.5, 1, 2 and 3 times the Redfield Ratio (Redfield, 1934) of carbon with respect to added PO_4. At regular 1-2 day intervals throughout each experiment, mesocosm water was sampled through silicon tubing immediately after mixing of the tanks using plastic paddles with the first 2 L discarded in order to flush the sample tubing.

A 3rd outdoor mesocosm experiment ~~(Taliarte~~, Gran Canaria, (Taliarte, March 2016) used 8 cylindrical polyurethane bags with a depth of approximately 3 m, a starting volume of ~8000 L and no lid or screen on top ~~(for further details see Filella et al., 2018 and Hopwood et al., 2018a)~~(for further details see Filella et al., 2018 and Hopwood et al., 2018a). After filling with coastal seawater the bags were allowed to stand for 4 days. A pH gradient across the 8 ~~tanks~~bags was then induced (on day 0), by the addition of varying volumes of filtered, pCO_2 saturated seawater (treatments outlined ~~Fig. S1 IV~~Supplementary Material) using a custom-made distribution device (Riebesell et al., 2013). A single macronutrient addition was made on day 18.

120

Label	Location	Month / year	Experiment duration / days	Manipulated drivers	Scale / L	Site	Design ~~(Fig. S1)~~	Fe data available
MesoPat ~~(Ocean Certain) Mesocosm~~	Comau fjord, Patagonia, 42.4° S 72.4° W	November 2014	11	DOC, grazing	1000	In-situ	I	Diurnal time series, Fe(II) decay experiments, XRF time series
~~MesoPat (Ocean Certain) Multistressor~~MultiPat	Comau fjord, Patagonia, 42.4° S 72.4° W	November 2014	8	DOC, grazing, pH	20	Temperature controlled room	II	Fe(II) decay experiments, XRF time series
MicroPat ~~MesoPat (Ocean Certain) Microcosm~~	Comau fjord, Patagonia, 42.4° S 72.4° W	November 2014	11	DOC, grazing	20	Temperature controlled room	III	Fe(II) decay experiments, XRF time series
MesoArc ~~(Ocean Certain) Mesocosm~~	Kongsfjorden, Svalbard, 78.9° N 11.9° E	July 2015	12	DOC, grazing	1250	In-situ	I	Fe(II) decay experiments, Diurnal time series, XRF time series
~~MesoArc (Ocean Certain) Multistressor~~MultiArc	Kongsfjorden, Svalbard, 78.9° N 11.9° E	July 2015	8	DOC, grazing, pH	20	Temperature controlled room	II	Fe(II) decay experiments

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Gran Canaria ~~(The Future Ocean) Mesocosm~~	Taliarte Harbour, Gran Canaria, 28.0° N 15.4° W	March 2016	28	pCO_2	8000	In-situ	IV	Mesocosm Fe(II) time series

Table ~~1A~~1 Details of experiments where Fe data were collected. Data from 6 separate experiments are presented, including 3 outdoor ~~mesocosm~~'meso'cosm experiments and 3 indoor ~~microcosm/multistressor~~'micro'cosm/'multi'stressor experiments. 'DOC' dissolved organic carbon~~, (glucose),~~ 'XRF' X-ray fluorescence spectroscopy. Designs are outlined in Supplementary Material.

Experiment	PAT (Patagonia)	ARC (Svalbard, Arctic)	Gran Canaria
~~Mesocosm~~'Meso'cosm	MesoPat-	MesoArc-	-Gran Canaria
Containers	HDPE 1000 L	HDPE 1250 L	Polyurethane 8000 L
Zooplankton ~~treatment~~addition for 'high' grazing	Addition of 30 copepods L^{-1}	Addition of 5 copepods L^{-1}	NA
Macronutrient addition	Nitrogen was added as NO_3	Nitrogen was added as NH_4	Nitrogen was added as NO_3
Macronutrient addition timing	Daily	Daily	Day 18 only
Macronutrients added (per addition)	1.0 µM NO_3, 1.0 µM Si, 0.07 µM PO_4	1.12 µM NO_3, 1.2 µM Si, 0.07 µM PO_4 (11.4 µM Si added on day 1)	3.1 µM NO_3, 1.5 µM Si, 0.2 µM PO_4
Screening of initial seawater	No screening	Screening by 200 µm	Screening by 3 mm
~~Multistressor~~'Multi'stressor	MultiPat	MultiArc	
Containers	HDPE collapsible 20 L	HDPE collapsible 20 L	
Zooplankton ~~treatment~~addition for 'high' grazing	Addition of 30 copepods L^{-1}	Addition of 5 copepods L^{-1}	
Light regime	15 h light / 9 h dark	24 h light	
Macronutrient addition	Same as Mesocosm	Same as Mesocosm	
Macronutrient addition timing	Daily	Daily	
Macronutrients added (per addition)	1.0 µM NO_3, 1.0 µM Si, 0.07 µM PO_4	1.12 µM NH_4, 1.2 µM Si, 0.07 µM PO_4	
pH post adjustment	7.54±0.09	7.76±0.03	
pH pre-adjustment	7.91±0.01	8.27±0.18	
Screening of initial seawater	Screening by 200 µm	Screening by 200 µm	
Temperature / ℃	13-18	4.0-7.0	
~~Microcosm~~'Micro'cosm	MicroPat		
Containers	HDPE collapsible 20 L		
~~Grazing treatment~~Zooplankton addition for 'high' grazing	Addition of 30 copepods L^{-1}		
Light regime	15 h light / 9 h dark		
Macronutrient addition timing	Daily		
Macronutrient addition	Nitrogen was added as NO_3		
Macronutrients added (per addition)	1.0 µM NO_3, 1.0 µM Si, 0.07 µM PO_4		

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Screening of initial seawater	Screening by 200 µm
Temperature / ℃	14-17

Table ~~1B~~2 Experiment details for each experiment. For ~~a visual representation of~~further details on experiment designs, the reader is referred to Supplementary Material. 'HDPE' high density polyethylene. Measured values are reported ± standard deviations.

2.2 Microcosm (MicroPat) and multistressor (MultiPat/MultiArc) set up and sampling

MicroPat, a 10-treatment microcosm mirroring the MesoPat 10 tank mesocosm (treatment design as per ~~Fig. S1 I~~MesoPat, but with 6 × 20 L containers per treatment rather than a single HDPE tank) and two 16-treatment multistressor experiments (~~Fig. S1 II~~MultiPat/MultiArc) were ~~also~~ conducted ~~as part of the Ocean Certain project,~~ using artificial lighting in temperature-controlled rooms (Table 1~~, Fig. S1~~). Coastal seawater, filtered through nylon mesh, was used to fill 20 L HDPE collapsible containers. The 20 L containers were arranged on custom made racks with a light intensity of 80 µmol quanta m^{-2} s^{-1}, approximating that at ~3 m depth. Lamps (Phillips, MASTER TL-D 90 De Luxe 36W/965 tubes) were selected to match the solar spectrum as closely as possible. A diurnal light regime representing spring/summer light conditions at each fieldsite was used and the tanks were agitated daily and after any additions (e.g. glucose, acid or macronutrient solutions) in order to ensure a homogeneous distribution of dissolved components. In all 20 L scale experiments, macronutrients were added daily. One 20 L container from each treatment set was 'harvested' for sample water each sampling day.

The experimental matrix used for the ~~two Ocean Certain multistressor~~MultiPat/MultiArc experiments duplicated the ~~Ocean Certain mesocosm~~MesoPat/MesoArc design, with an additional pH manipulation: ambient and low pH. The pH of 'low' pH treatments was adjusted by a single addition of HCl (trace metal grade) on day 0 only with pH measured prior to and after the addition (Table ~~1~~2). Sample water from 20 L collapsible containers was extracted using a plastic syringe and silicon tubing which was mounted through the lid of each collapsible container.

Throughout, where changes in ~~mesocosms/microcosms~~meso/micro/multi experiments are plotted against time, 'day 0' is defined as the day the experimental gradient (zooplankton, DOC, pH, pCO_2) was imposed. Time prior to day 0 was intentionally introduced during some experiments to allow water to equilibrate with ambient physical conditions after mesocosm filling. Fe(II) concentration varies on diurnal timescales and thus during each experiment where a time series of Fe(II) or DFe concentration was measured, sample collection and analysis occurred at the same time each day.

2.3 Chemical analysis

Trace elements

Trace metal clean low density polyethylene (LDPE, Nalgene) bottles were prepared via a three stage washing procedure~~:~~ (1 day in detergent, 1 week in 1.2 M HCl, 1 week in 1.2 M HNO_3~~.~~) and then stored empty and double bagged until use. Total dissolvable Fe (TdFe) samples were collected without filtration in trace metal clean 125 mL LDPE bottles. Dissolved Fe

(DFe) samples were collected in 0.5 or 1 L trace metal clean LDPE bottles and then filtered through acid-rinsed 0.2 µm filters (PTFE, Millipore) using a peristaltic pump (Minipuls 3, Gilson) into trace metal clean 125 mL LDPE bottles within 4 h of sample collection. TdFe and DFe samples were then acidified to pH <2.0 by the addition of HCl (150 µL, UpA grade, Romil) and stored for 6 months prior to analysis. Samples were then diluted using 1 M distilled HNO_3 (SpA grade, Romil, distilled using a sub-boiling PFA distillation system, DST-1000, Savillex) and subsequently analyzed by high resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS, ELEMENT XR, ThermoFisherScientific) with calibration by standard addition. To verify the accuracy of Fe measurements the Certified Reference Materials NASS-7 and CASS-6 were analysed after the same dilution procedure with the measured Fe concentration in close agreement with certified values (6.21 ± 0.77 nM certified 6.29 ± 0.47 nM, and 26.6 ± 0.71 nM certified 27.9 ± 2.1 nM). The analytical blank was 0.13 nM Fe. The field blank (de-ionized, MilliQ, water handled and filtered as if a sample in the field) was ~0.5 nM and varied slightly between ~~mesocosms~~field experiments, yet was always <16% of DFe concentration.

Fe(II) samples (unfiltered) were collected in trace metal clean translucent 50 or 125 mL LDPE bottles~~, transferred to a clean laboratory~~ and analyzed via flow injection analysis (FIA) using luminol chemiluminescence without preconcentration (Croot and Laan, 2002) exactly as per Hopwood et al., (2017a). Fe(II) samples during the ~~Ocean Certain~~MesoPat/MesoArc/MicroPat/MultiPat/MultiArc experiments were analysed immediately after sub-sampling from each individual mesocosm/microcosm/multistressor container. In Gran Canaria the warmer seawater temperature and distance between the experiment location and laboratory precluded immediate analysis. Therefore, prior to sampling, 10 µL 6 M HCl (Hiperpur-Plus) was added to the LDPE bottles in order to maintain the sampled seawater at pH 6 and thus minimize oxidation of Fe(II) between sample collection and analysis~~; a~~. For Gran Canaria only, opaque LDPE bottles were used to prevent further photochemical formation of Fe(II). The pH modification is outlined in detail by Hansard and Landing (2009)~~.~~ and is not thought to significantly affect in-situ Fe(II) concentrations during the short time period between collection and analysis. Fe(II) was then quantified within 2 h of sample collection. In all cases Fe(II) was calibrated by standard additions (normally from 0.1-2 nM) using 100 or 600 µM stock solutions. Stock solutions were prepared from ammonium Fe(II) sulfate hexahydrate (Sigma-Aldrich), acidified with 0.01 M HCl and stored in the dark. A diluted Fe(II) stock solution (1-2 µM) was prepared daily. The detection limit varied slightly between FIA runs from 90 pM (Gran Canaria) to 200 pM (Arc/Pat experiments~~MesoArc/MesoPat~~).

~~Wavelength dispersive X-ray fluorescence (WDXRF) was conducted on triplicates of particulate samples collected by filtering 500 mL of seawater through 0.6 µm polycarbonate filters. After air drying overnight, samples were stored in PetriSlide boxes at room temperature until analysis at the University of Bergen (Norway). Analysis via WDXRF spectroscopy was exactly as described by (Paulino et al., 2013) using a S4 Pioneer (Bruker AXS, Karlsruhe, Germany).~~

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Wavelength dispersive X-ray fluorescence (WDXRF) was conducted on triplicates of particulate samples collected by filtering 500 mL of seawater through 0.6 µm polycarbonate filters. After air-drying overnight, samples were stored in PetriSlide boxes at room temperature until analysis at the University of Bergen (Norway). Analysis via WDXRF spectroscopy was exactly as described by Paulino et al., (2013) using a S4 Pioneer (Bruker-AXS, Karlsruhe, Germany).

Macronutrients and chlorophyll a

Dissolved macronutrient concentrations (nitrate, phosphate, silicic acid; filtered at 0.45 µm) were measured spectrophotometrically the same day as sample collection (Hansen and Koroleff, 2007). ~~For experiments in Crete, phosphate concentrations were determined using the 'magic' method (Rimmelin and Moutin, 2005) because of the ultralow concentrations.~~ Nutrient detection limits inevitably varied slightly between the different mesocosm/microcosm/multistressor experiments, however this does not adversely affect the discussion of results herein. Chlorophyll a was measured by fluorometry as per Welschmeyer (1994).

Carbonate chemistry

pH (except where stated otherwise, 'pH' refers to the total scale reported at 25ºC) was measured during the Gran Canaria mesocosm using the spectrophotometric technique of Clayton and Byrne (1993) with m-cresol purple in an automated Sensorlab SP101-SM system and a 25ºC-thermostatted 1 cm flow-cell exactly as per González-Dávila et al., (2016). pH during ~~the~~ MesoPat ~~experiments~~/MicroPat/MultiPat was measured similarly as per Gran Canaria using m-cresol. During MesoArc ~~experiments~~/MultiArc pH was measured spectrophotometrically as per Reggiani et al., (2016). For calculation of Fe(II) oxidation rates constants as per Santana-Casiano et al., (2005), pH_{free} was calculated from measured pH using the sulphate dissociation constants derived from Dickson (1990).

2.4 In-situ biogeochemical parameters

Fe(II) concentrations, and other key biogeochemical parameters, were measured in ambient surface (~10-20 cm depth) water at all three experiment locations; Comau fjord for Meso/Micro/MultiPat (Patagonia, November 2014), Kongsfjorden for Meso/MultiArc (Svalbard, June 2015) and Taliarte (Gran Canaria, March 2016). FIA apparatus was assembled in waterproof boxes on floating jetties. A 3 m PTFE sample line was then positioned to float approximately 1 m away from the jetty with seawater constantly pumped into the FIA using a peristaltic pump (MiniPuls 3, Gilson). The time delay between water inflow into the PTFE line and sample analysis was 60-120 s. The concentrations of complimentary chemical parameters (TdFe, DFe, DOC, pH) were determined on samples collected by hand using trace metal clean 1 L LDPE bottles. Salinity and temperature data was collected with a hand-held LF 325 conductivity meter (WTW) calibrated with KCl solution. To compare Fe(II)/H_2O_2 FIA data to discrete DFe/TdFe samples the mean of 7 FIA datapoints, corresponding to 14 minutes of sample intake and analysis time, was used.

2.5 Fe(II) decay experiments

A series of experiments was conducted ~~in Patagonia, Svalbard,~~during Meso/Micro/MultiPat, Meso/MultiArc (n=79), and under laboratory conditions ~~in Kiel~~using filtered Atlantic seawater (n=46) to investigate the change in Fe(II) concentration when water was moved from ambient light into the dark. Fe(II) decay experiments were conducted inside the temperate controlled rooms hosting the MultiPat/MultiArc experiments. As such, a constant temperature was maintained throughout these experiments. Sub-samples for Fe(II) analysis or decay experiments were always collected when the mesocosms had been untouched (i.e. no sampling or additions) for >12 h, thus Fe(II) species could not plausibly have been directly perturbed by any external manipulation of the mesocosm/microcosm~~In Patagonia and Svalbard,~~/multistressor experiments. After collection of unfiltered 1-2 L samples in transparent 2 L HDPE containers, the PTFE FIA sample line was placed into the sample bottle and continuous analysis for Fe(II) and H_2O_2 begun. After a stable chemiluminescence response was obtained (typically 2-4 ~~min~~minutes after first loading the sample), the sample bottle was moved to ~~a~~an Al foil lined dark laminar flow hood and analysis continued for >1 h or until Fe(II) concentration fell below the detection limit (~0.2 nM). The time at which the sample was moved into the dark was designated t = 0. Subsamples for the determination of DFe and TdFe were retained from this time point.

Theoretical decay rate constants (k') for these experiments were calculated using the formulation presented in Santana-Casiano et al., (2005) with measured pH, temperature, dissolved O_2 and salinity as per Eq. (1) where T is temperature (°K), pH is pH_{free} and S is salinity (psu). O_2 saturation was calculated as per Garcia and Gordon (1992) and then k' was adjusted for measured O_2 concentrations as per Eq. (2). Measured rate constants (k_{meas}) were derived from the gradient of ln[Fe(II)] against time for each decay experiment from at least 5 sequential datapoints (Fe(II) concentration was obtained at 2 minute intervals).

$$\text{Equation 1} \quad logk' = 35.407 - \left(6.7109 \times pH_{free}\right) + \left(0.5342 \times pH_{free}^2\right) - \left(\frac{5362.6}{T}\right) - (0.04406 \times S^{0.5}) - (0.002847 \times S)$$

$$\text{Equation 2} \quad k = \frac{k'}{[O_2]}$$

~~(see s3.5).~~ Dissolved oxygen was measured using an Oxyminisensor (World Precision Instruments). Salinity and temperature for each experiment were measured using a hand-held LF 325 conductivity meter (WTW). Measured decay rates were determined, assuming pseudo-first order kinetics, from linear regression of ln[Fe(II)] for t 0-15 minutes. Fe(II) decay experiments under laboratory conditions used aged, filtered (0.2 µm) Atlantic water. This water was previously stored filtered in 1 m^3 trace element clean HDPE containers for in excess of 1 year and maintained in the dark at experimental temperature for 3 days prior to commencing any experiment.

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2.6 Quantifying the potential for Fe contamination during a mesocosm experiment

During ~~the~~ MesoArc ~~mesocosm (Svalbard)~~ a 'bookkeeping' exercise was conducted for the mesocosm ~~and multistressor experiments~~experiment by the sub-sampling of all solutions added to the incubated seawater. Aqueous additions consisted of: HCl solution (used to apply the pH gradient), macronutrient solution, glucose solution and zooplankton. A short (1-2 h) 1 M HCl (trace metal grade) leach was applied to equipment placed within the mesocosm and also to the HDPE mesocosm containers prior to filling to provide a quantitative estimate of 'leachable' Fe. Atmospheric deposition of Fe into the tanks when open was estimated by deploying open bottles of de-ionized water within the vicinity of the mesocosms for fixed time intervals of 1 h in triplicate on 3 occasions and recording the approximate extent of time when the mesocosm lids were removed. All additions to the MesoArc mesocosm experiment were volume weighted as per Eq. (3) using the mean (mid-experiment) mesocosm volume ($V_{mesocosm}$), and assuming that all additions were well mixed and TdFe behaved conservatively.

Equation 3 $$\Delta[TdFe]_{mesocosm} = \frac{V_{addition}}{V_{addition} + V_{mesocosm}} \times [TdFe]_{addition}$$

Results

~~**Results**~~

3.1 'Bookkeeping' Fe additions for a 1000 L mesocosm experiment (MesoArc)

In order to provide a rigorous assessment of Fe contamination during one experiment, Fe inputs were tracked in all additions to MesoArc and scaled to the mesocosm volume (initially 1200 L, declining by 15% over the experiment duration).Volume weighting all additions (Table 3) to the MesoArc mesocosm experiment as per Eq. (3) produced a total mean concentration of 48 nM TdFe (Fig. 1). In addition to the uncertain variability arising as the mesocosms were filled, approximately 8% (3.6 nM) of TdFe within the MesoArc experiment could be attributed to inadvertent addition (Fig. 1) over the experiment duration.

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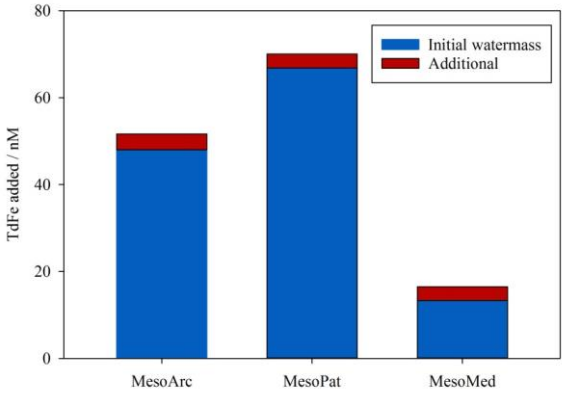

Figure 1: Volume-weighted additions of TdFe to the same experimental design at threemesocosm experiments. For MesoArc all inputs to the mesocosm were explicitly quantified. For MesoPat/MesoMed the initial water mass TdFe was quantified and TdFe inputs were adjusted as if the MesoArc experiment had been exactly duplicated with only the initial water mass changed.

When MesoArc is compared to the two other mesocosms with a similar design (MesoPat and MesoMed) the TdFe inputs and the relative contribution of inadvertent TdFe addition were: 66.9 nM TdFe with 4.8% arising from inadvertent addition for MesoPat and 13.3 nM with 24% TdFe arising from inadvertent addition for MesoMed (Fig. 1). Systematic contamination was in all cases a minor, yet measurable, source of TdFe for these inshore mesocosms. Strictly, the inadvertent input of TdFe varied between different treatments within each mesocosm experiment due to, for example, the variable volume of glucose solution used to create a DOC gradient (Table 1). However, these differences caused small or negligible changes in TdFe addition (Table 3).

Fe source	**TdFe addition / nM**
Macronutrient spikes[a]	<0.01
Glucose spikes[a]	<0.01
Equipment added to mesocosms	0.14 ± 0.04
Zooplankton addition	0.55 ± 0.01
Atmospheric deposition	0.87 ± 0.99
Mesocosm plastic surfaces	2.1 ± 0.54
Combined contamination and watermass variability	*4-10% of initial [TdFe]*

during filling (percentage of initial TdFe)[b]	

Table 3. Total dissolvable Fe (TdFe) additions to the MesoArc mesocosm containers associated with sources other than the initial watermass.[a] These TdFe concentrations were measurable, but negligible when scaled to the mesocosm volume.[b] Based on TdFe measurements at time zero from the MesoPat multistressor/microcosm and DSi measurements on experiment day 0 or 1 from multiple mesocosms.

3.2 General trends in Fe biogeochemistry; the MesoArc and MesoPat mesocosms

Concentrations of both DFe and H_2O_2 (as per Hopwood, 2018) were measured at the highest resolution for the baseline treatments (no DOC addition, no zooplankton addition) during the mesocosm experiments. For MesoPat (Fig. 2), the initial concentration of DFe and H_2O_2 was estimated by using a Go-Flo bottle to sample at a depth of 10 m in the fjord (at which approximate depth the mesocosms were filled from). The apparent rise in H_2O_2 between day 0 and day 1 (Fig. 2) likely reflects the result of increased formation of H_2O_2 after pumping of water from ~10 m depth into containers at the surface. NO_3 was added daily (Table 2), hence concentrations increased prior to the onset of a phytoplankton bloom. The decline in DFe likely reflects biological uptake and/or scavenging onto particle (>0.2 µm) or mesocosm container surfaces.

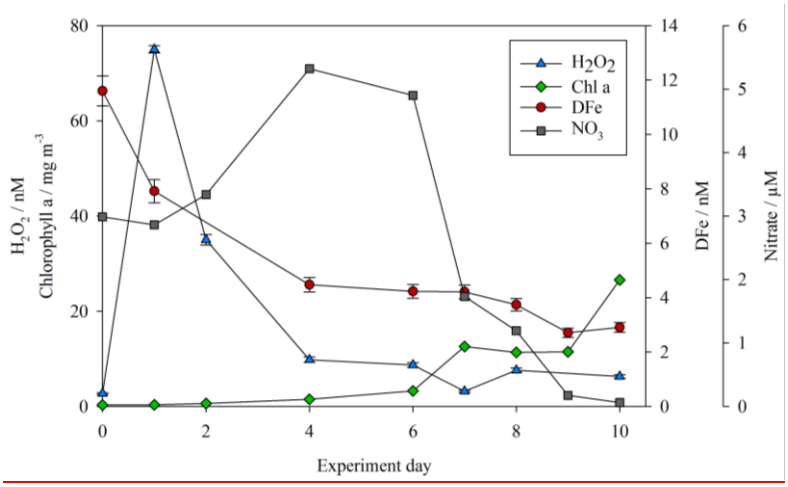

Figure 2: DFe (red circles), hydrogen peroxide (H_2O_2, blue triangles), nitrate (NO_3, grey squares) and chlorophyll a (green diamonds) for the baseline treatment (no DOC addition, no added zooplankton) during the MesoPat mesocosm.

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Less frequent temporal resolution was available for treatments other than the 'baseline' no DOC/zooplankton addition treatment, but the decline in DFe during the MesoPat mesocosm was apparent across all measurements considered together. In addition to TdFe measurements from unfiltered water samples, particulate (>0.6 µm) Fe concentrations were also determined from wavelength dispersive X-ray fluorescence. WDXRF data were normalised to phosphorus (P) in order to discuss trends in the elemental composition of particles and are thus presented as the Fe:P [mol Fe mol^{-1} P] ratio. The initial

Fe:P ratio in particles varied between the mesocosm fieldsites: MesoPat 0.34 ± 0.09 and MesoArc 0.62 ± 0.07. A similar trend however was observed during all experiments; a general decline in Fe:P across all treatments with time. Particulate Fe:P ratios on the final day of measurements was invariably lower than the initial ratio: MesoPat 0.09 ± 0.04, MicroPat 0.05 ± 0.01, MultiPat 0.07 ± 0.03, and MesoArc 0.17 ± 0.08. All of these ratios are high compared to literature values reported for offshore stations where the ratio for cellular material ranged from 0.005 to 0.03 mol Fe mol^{-1} P (Twining and Baines, 2013). However, this may simply reflect elasticity in Fe:P ratios which increase under high DFe conditions (Sunda et al., 1991; Sunda and Huntsman, 1995). Alternatively, it could reflect the inclusion of a large fraction of lithogenic material, which would be expected to have a higher Fe:P ratio than biogenic material (Twining and Baines, 2013).

Particles from ambient waters outside the mesocosms were collected and analysed at the Patagonia and Svalbard fieldsites in order to assist in interpreting the temporal trend in Fe:P. Suspended particles from Kongsfjorden (Svalbard) exhibited a Fe:P ratio of 3.01 ± 0.06 mol Fe mol^{-1} P and suspended particles in Comau fjord (Patagonia) varied more widely with a mean ratio of 0.54 ± 0.41. Kongsfjorden surface waters are characterised by extremely high TdFe concentrations originating from particle rich meltwater plumes (Hop et al., 2002) and thus the 3.0 Fe:P ratio can be considered to be a lithogenic signature. After ambient water was collected for the mesocosm experiments, the steady decline in particle Fe:P ratios throughout the experiments likely resulted partially from a settling or aggregation of lithogenic material after filling of the mesocosms. At the same time, a decline in the ratio of dissolved Fe:PO_4 during each experiment, due to the daily addition of PO_4 and minimal addition of new Fe, may also have led to reduced Fe uptake relative to P.

3.4 Fe(II) time series (Gran Canaria)

A key focus of this work was to determine the fraction of DFe present as Fe(II). During the Gran Canaria mesocosm, a detailed time series of Fe(II) concentrations was conducted. The timing of sample collection was the same daily (14:30 UTC) in order to minimise the effect of changing light intensity over diurnal cycles on measured Fe(II) concentrations. Over the duration of the Gran Canaria mesocosm, Fe(II) concentrations fell within the range 0.10-0.75 nM (Fig. 3a). On the first measured day (day -2) Fe(II) ranged from 0.13 nM (mesocosm 7, 700 µatm pCO_2) to 0.63 nM (mesocosm 6, 1450 µatm pCO_2) with an overall mean (± standard deviation) concentration of 0.41 ± 0.12 nM. From day 9 to 20 strong variations were observed between treatments. Following nutrient addition on day 18, a phytoplankton bloom was evident in chlorophyll a data from day 19 or 20 with chlorophyll a peaking on day 21 or later (Hopwood et al., 2018b). An increase in Fe(II) was then evident from days 20-29 under bloom and post-bloom conditions (Fig. 3b).

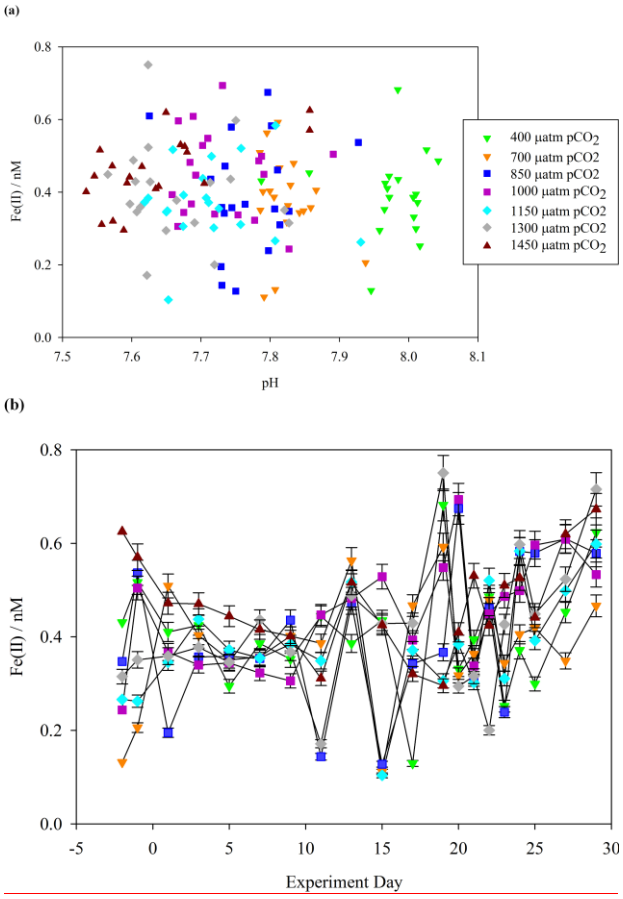

Figure 3: (a) Fe(II) concentrations (unfiltered) during the Gran Canaria mesocosm plotted against measured mesocosm pH (b) Fe(II) concentrations over the duration of the Gran Canaria mesocosm experiment. The 550 µatm pCO_2 mesocosm was discontinued after leakage and exchange with surrounding seawater occurred on experiment day 3 and so no data is shown.

Contrasting days 1 and 29, Fe(II) in all of the mesocosms except the 700 µatm pCO_2 treatment experienced a measurable increase in Fe(II) concentration (+0.4, +0.4, +0.2, +0.2, +0.2, 0.0 and +0.3 nM). The 700 µatm pCO_2 treatment was also anomalous with respect to slow post-bloom nitrate drawdown and elevated H_2O_2 concentration (100 nM H_2O_2 greater than other treatments under post-bloom conditions (Hopwood et al., 2018b)). Overall, despite the large gradient in pCO_2 (400-1450 µatm and a corresponding measured pH range of 8.1-7.7), Fe(II) showed no significant correlation with pH (Pearson Product Moment Correlation p 0.32) (Fig. 3a).

3.5 Fe(II) decay experiments (Meso/micro/multiPat and Meso/multiArc)

In a companion text presenting H_2O_2 results from the same series of experiments (Hopwood et al., 2018a), a series of experiments in the Mediterranean (MesoMed/MultiMed) is also included. During these Mediterranean experiments however the rapid oxidation rate of Fe(II) precluded the determination of Fe(II) concentrations. Fe(II) concentrations were universally <0.2 nM (i.e. below detection) and thus no Fe(II) results from the 'Med' experiments are presented herein. During the MesoArc and MesoPat experiments, a series of decay experiments was conducted to investigate the stability of in-situ Fe(II) concentrations. The 79 time points at the start of these experiments were made before water was moved from ambient lighting into the dark and can be considered as in-situ Fe(II) concentrations. Across the complete dataset, the properties known to affect the rate of Fe(II) oxidation in seawater varied over relatively large ranges for the various experiments; temperature 4.0-18°C, salinity 22.7-33.8, pH 7.46-8.44, 315-449 µM O_2, and 1-79 nM H_2O_2 (see Supplementary Material). Initial Fe(II) concentrations ranged from 0.3-16 nM. Generally a decline in Fe(II) was observed immediately after transferring this sampled water to a dark box, yet this was not always the case. The Fe(II) concentration more often than not remained measurable (> 0.2 nM) for the entire duration of the decay experiment. One hour after the transfer of water from ambient conditions into the dark, Fe(II) was below detection on only 2 out of 79 occasions, and on average 55% of the initial Fe(II) concentration at t = 0 remained.

In order to account for the many physio-chemical parameters that affect Fe(II) oxidation rates, theoretical pseudo-first order rate constants (k') were calculated for each decay experiment assuming pseudo-first order kinetics (correlation coefficients are noted for each linear regression- Supplementary Material). The rate constant, k (Eq. 1), thus accounts for the major effect of variations between experiments of salinity, temperature, pH and O_2 in a single constant (Fig. 4). Before comparing k_{meas} and k, an estimate of the uncertainty should also be made as differences between the two values may arise due to the relatively large combined error from propagating the uncertainty in $S/T/pH_{free}/[O_2]$, and in analytical error on Fe(II) measurements. The accuracy of Fe(II) measurements is challenging to quantify for a transient species with no appropriate reference material. In this case, the exact Fe(II) detection method used here was previously compared to another variation of the luminol chemiluminescence method (with pre-concentration, Bowie et al., 2002b)) and k_{meas} was determined with ±20% difference between two methods. The uncertainty on k_{meas} is therefore assumed to be ±20% rather than the generally smaller uncertainty than can be calculated from linear regression of ln[Fe(II)]. The uncertainty in calculated k was assessed by calculating the change resulting from the estimated uncertainty on measured salinity (±0.1), temperature (±0.5°C), pH_{free} (±0.05) and O_2 (±10 µM). The combined uncertainty is ±35% for k. Reduced uncertainties are possible with closed thermostat systems where the uncertainty on all physical/chemical parameters ($S/T/pH/O_2$) would be reduced, however our objective here was to measure the decay rates of in situ Fe(II) concentrations and thus the first priority was to commence measurements after sub-sampling rather than to stabilize physical/chemical conditions.

In order to further understand the cause of any systematic discrepancies in the dataset between measured k_{meas} and calculated k, an additional set of experiments was conducted using aged, filtered Atlantic seawater (Fig. 4). The background concentration of Fe(II) in this water was below detection (<0.2 nM) and the initial DFe concentration relatively low (0.98 ± 0.39 nM). In a series of 46 decay experiments, Fe(II) spikes of 2-8 nM were added and then the decay in the dark monitored as per the Meso/micro/multi Arc/Pat in-situ experiments.

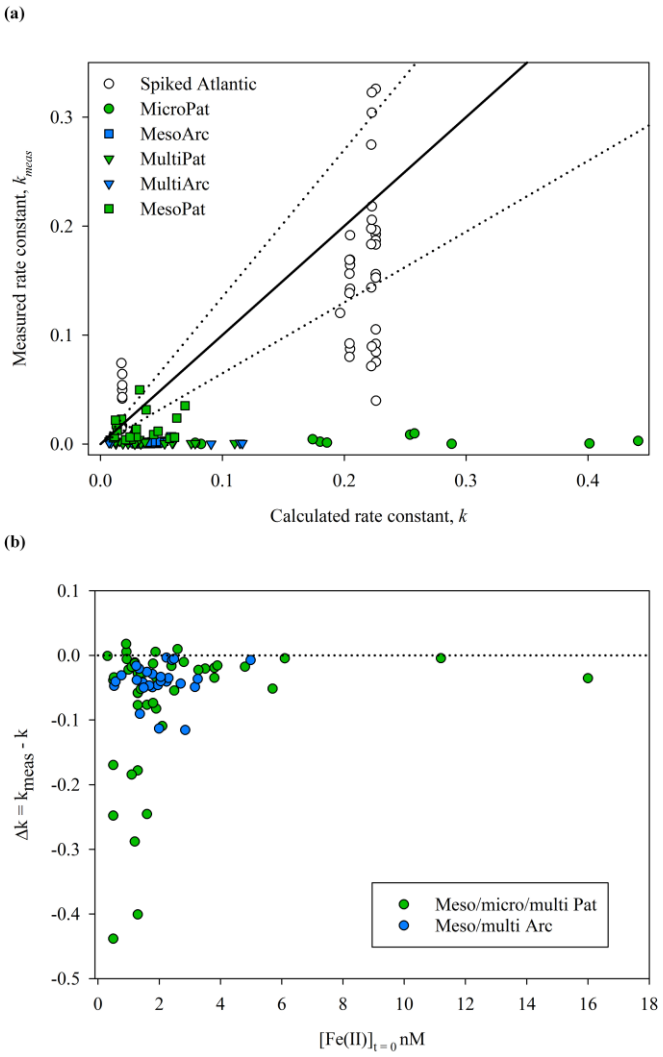

Figure 4: A comparison of k_{meas} and calculated k (both M^{-1} min^{-1}) for Fe(II) decay experiments. (a) Rate constants for Fe(II) decay experiments from Meso/micro/multiPat (green), Meso/multiArc (blue) and spikes to aged Atlantic seawater (colourless) (b) The difference between observed and calculated values of k ($\Delta k = k_{meas}$-k) is shown against Fe(II) concentration at t = 0 minutes.

4 Discussion

4.1 Assessing the extent of Fe contamination within a mesocosm experiment (MesoArc)

Assembling and maintaining mesocosm scale experiments under trace-element clean conditions is a logistically challenging exercise (e.g. Guieu et al., 2010) and thus it was desirable to conduct a thorough assessment of the extent to which Fe concentrations were subject to inadvertent increases during at least one experiment. ~~It could not normally be determined directly and reliably how much inadvertent contamination occurred during the filling of the mesocosm containers because the filling procedure typically occurred over approximately 12-24 h duration. The Fe concentration in the near-shore water used to fill all of the mesocosms likely varied substantially over this time period due to wind and tidal water displacement in addition to variable surface runoff. Also, the mesocosms could not be sampled using trace metal clean conditions immediately after (or during) filling.~~

~~In order to provide a rigorous assessment of Fe contamination during one experiment, Fe inputs were tracked in all additions to the MesoArc mesocosm and scaled to the mesocosm volume (initially 1200 L, declining by 15% over the experiment duration). Both DFe and TdFe were determined. However, DFe in seawater does not behave conservatively under most circumstances due to the low solubility of Fe(III) and rapid scavenging of DFe from the water column (Landing and Bruland, 1987; Liu and Millero, 2002). TdFe concentration, on the other hand, can at least be used to assess the relative importance of 'inadvertent' Fe addition to the mesocosm. Volume weighting all additions (Table 2) to the MesoArc mesocosm experiment as per Eq. (1) using the mean (mid-experiment) mesocosm volume ($V_{mesocosm}$), and assuming that all additions were well mixed and TdFe behaved conservatively, produced a total mean concentration of 48 nM TdFe (Fig. 1). In addition to the uncertain variability arising as the mesocosms were filled, approximately 8% (3.6 nM) of TdFe within the MesoArc mesocosms could be attributed to inadvertent addition (Fig. 1) over the experiment duration.~~

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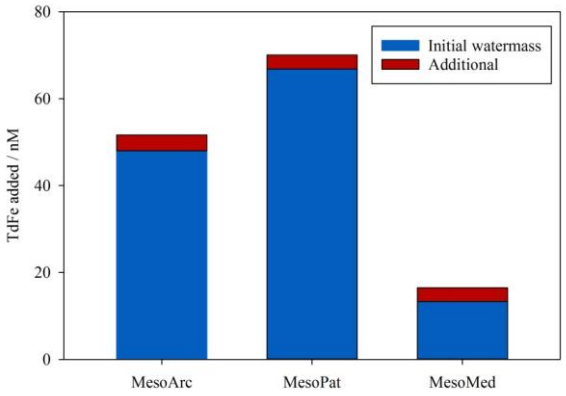
~~Equation 1~~ $$\Delta[TdFe]_{mesocosm} = \frac{V_{addition}}{V_{addition} + V_{mesocosm}} \times [TdFe]_{addition}$$



~~**Figure 1: Volume-weighted additions of TdFe to the same experimental design at three Ocean Certain mesocosm experiments. For MesoArc all inputs to the mesocosm were explicitly quantified. For MesoPat/MesoMed the initial water-mass TdFe was quantified and TdFe inputs were adjusted as if the MesoArc experiment had been exactly duplicated with only the initial water-mass changed.**~~

~~When MesoArc is compared to the two other mesocosms with a similar design (MesoPat and MesoMed) the TdFe inputs and the relative contribution of inadvertent TdFe addition were: 66.9 nM TdFe with 4.8% arising from inadvertent addition for MesoPat and 13.3 nM with 24% TdFe arising from inadvertent addition for MesoMed (Fig. 1). Systematic contamination was in all cases a minor, yet measurable, source of TdFe for these inshore mesocosms. Strictly, the inadvertent input of TdFe varied between different treatments within each mesocosm experiment due to, for example, the variable volume of glucose solution used to create a DOC gradient (Table 1). However, these differences caused small or negligible changes in TdFe addition. It is not anticipated that this small TdFe addition will have had any adverse effect on the Fe redox chemistry results presented herein for the Arctic and Patagonia experiments. As an additional precaution, Sub-samples for Fe(II) analysis or decay experiments were always collected when the mesocosms had been untouched (i.e. no sampling or additions) for >12 h, thus Fe(II) species could not plausibly have been directly perturbed by any external manipulation of the mesocosm/microcosm experiments.~~

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Fe source	TdFe addition / nM
Macronutrient spikes[a]	<0.01
Glucose spikes[a]	<0.01
Equipment added to mesocosms	0.14 ± 0.04
Zooplankton addition	0.55 ± 0.01
Atmospheric deposition	0.87 ± 0.99
Mesocosm plastic surfaces	2.1 ± 0.54
Combined contamination and watermass variability during filling (percentage of initial TdFe)[b]	*4-10% of initial [TdFe]*

Table 2. Total dissolvable Fe (TdFe) additions to the MesoArc mesocosm containers associated with sources other than the initial watermass.[a] These TdFe concentrations were measurable, but negligible when scaled to the mesocosm volume.[b] Based on TdFe measurements at time zero from the MesoPat multistressor/microcosm and DSi measurements on experiment day 0 or 1 from multiple mesocosms.

3.2 General trends in Fe biogeochemistry; the MesoArc (Svalbard) and MesoPat (Patagonia) mesocosms

Before presenting the results of experiments designed to investigate the concentrations and stability of Fe(II), an over view of Fe biogeochemistry within the different experiments is given. For all paired DFe/TdFe datapoints available during the MesoArc/MesoPat experiments (Fig. 2) the linear correlation between DFe and TdFe was not strong with most experiments maintaining a DFe concentration of 3-9 nM irrespective of TdFe. Curiously though, the correlation between DFe and TdFe was stronger for MesoArc than for MesoPat (MesoPat R^2 0.0022, gradient 0.0049 ± 0.014; MesoArc R^2 0.48 gradient 0.036 ± 0.0073).

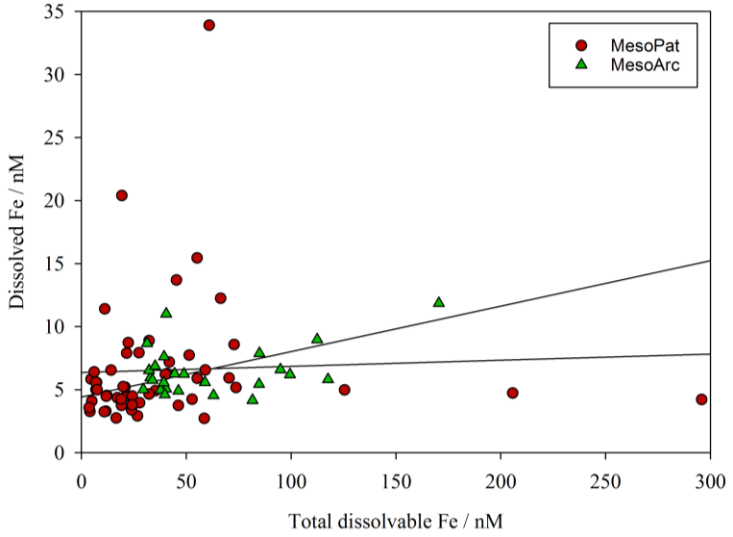

Figure 2: DFe and TdFe from the MesoPat and MesoArc mesocosm and multistressor experiments where samples for both parameters were collected at the same timepoint. Linear regressions shown for MesoArc (R^2 0.48 gradient 0.036 ± 0.0073) and MesoPat (R^2 0.0022, gradient 0.0049 ± 0.014).

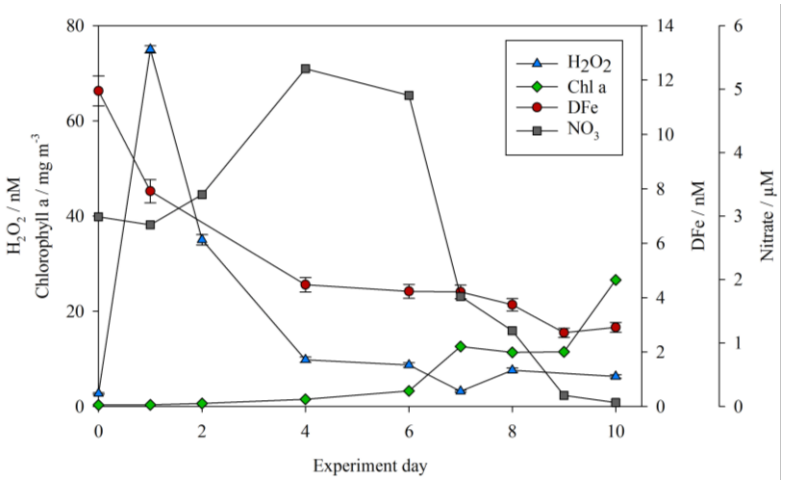

Figure 3: DFe (red circles), hydrogen peroxide (H_2O_2, blue triangles), nitrate (NO_4, grey squares) and chlorophyll a (green diamonds) for the baseline treatment (no DOC addition, no added zooplankton) during the MesoPat mesocosm.

Concentrations of both DFe and H_2O_2 (as per Hopwood, 2018) were measured at the highest resolution for the baseline treatment (no DOC addition, no zooplankton addition) during the MesoPat mesocosm. the initial concentration of DFe and H_2O_2 was estimated by using a Go-Flo bottle to sample at a depth of 10 m in the fjord (at which approximate depth the mesocosms were filled from). The apparent rise in H_2O_2 between day 0 and day 1 (Fig. 3) likely reflects the result of increased formation of H_2O_2 after pumping of water from ~10 m depth into containers at the surface. NO_3 was added daily (Table 1b), hence concentrations increased prior to the onset of a phytoplankton bloom. The decline in DFe likely reflects biological uptake and/or scavenging onto particle (>0.2 µm) or mesocosm container surfaces.

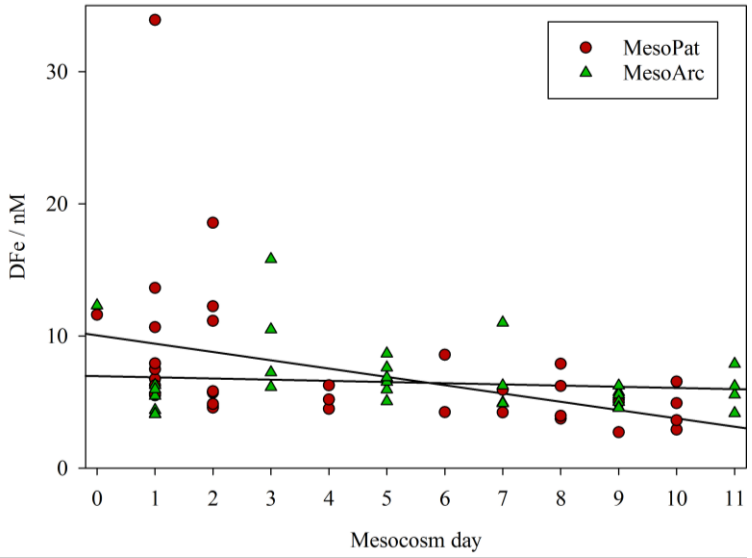

Figure 4: DFe for all measurements made from the MesoPat (red circles) and MesoArc (green triangles) mesocosm experiments against time. Linear regressions exclude the day 0 datapoints which were estimated from fjord water during mesocosm filling and therefore were not strictly comparable to measurements within the mesocosms.

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Less frequent sampling for dissolved trace elements was available for treatments other than the 'baseline' no DOC/zooplankton addition treatment, but the decline in DFe during the MesoPat mesocosm was apparent across all measurements considered together (0.63 ± 0.24 nM day^{-1} derived from linear regression R^2 0.16, Fig. 4). When all available MesoArc DFe data was compiled similarly, the DFe concentration was steady over the duration of the mesocosm (0.09 ± 0.13 nM day^{-1} derived from linear regression R^2 0.016, Fig. 4).

In addition to TdFe measurements from unfiltered water samples, particulate (>0.6 µm) Fe concentrations were also determined from wavelength dispersive X-ray fluorescence. WDXRF data were normalised to phosphorus (P) in order to

discuss trends in the elemental composition of particles and are thus presented as the Fe:P [mol Fe mol^{-1} P] ratio. The initial Fe:P ratio in particles varied between the three mesocosm fieldsites: MesoMed 1.20 ± 0.34, MesoPat 0.34 ± 0.09 and MesoArc 0.62 ± 0.07. A similar trend however was observed during all experiments; a general decline in Fe:P across all treatments with time. Particulate Fe:P ratios on the final day of measurements was invariably lower than the initial ratio: MesoMed 0.16 ± 0.04, MesoPat 0.09 ± 0.04, MicroPat 0.05 ± 0.01, MultiPat 0.07 ± 0.03, and MesoArc 0.17 ± 0.08. All of these ratios are high compared to literature values reported for offshore stations where the ratio ranged from 0.005 to 0.03 mol Fe mol^{-1} P (Twining and Baines, 2013). However, this may simply reflect elasticity in Fe:P ratios which increase under high DFe conditions (Sunda et al., 1991; Sunda and Huntsman, 1995; Twining and Baines, 2013). Alternatively, it could reflect the inclusion of a large fraction of lithogenic material, which would be expected to have a higher Fe:P ratio than biogenic material.

Particles from ambient waters outside the mesocosms were collected and analysed at the Patagonia and Svalbard fieldsites in order to assist in interpreting the temporal trend in Fe:P. Suspended particles from Kongsfjorden (Svalbard) exhibited a Fe:P ratio of 3.01 ± 0.06 mol Fe mol^{-1} P and suspended particles in Comau fjord varied more widely with a mean ratio of 0.54 ± 0.41. Kongsfjorden surface waters are characterised by extremely high TdFe concentrations originating from particle rich meltwater plumes and thus the 3.0 Fe:P ratio can be considered to be a lithogenic signature. After ambient water was collected for the mesocosm experiments, the steady decline in particle Fe:P ratios throughout the experiments likely resulted partially from a settling or aggregation of lithogenic material after filling of the mesocosms. At the same time, a decline in the ratio of dissolved Fe:PO_4 during each experiment, due to the daily addition of PO_4 and minimal addition of new Fe, may also have led to reduced Fe uptake relative to P.

3.4 Fe(II) time series (Gran Canaria)

A key focus of this work was to determine the fraction of DFe present as Fe(II). During the Gran Canaria mesocosm, a detailed time series of Fe(II) concentrations was conducted. The timing of sample collection was the same daily (14:30 UTC) in order to minimise the effect of changing light intensity over diurnal cycles on measured Fe(II) concentrations. Over the duration of the Gran Canaria mesocosm, Fe(II) concentrations fell within the range 0.10-0.75 nM (Fig. 5 (a)). On the first measured day (day -2) Fe(II) ranged from 0.13 nM (mesocosm 7, 700 µatm pCO_2) to 0.63 nM (mesocosm 6, 1450 µatm pCO_2) with an overall mean concentration of 0.41 ± 0.12 nM. Generally, Fe(II) concentrations declined across all treatments from day 1 to 9. From day 9 to 20 strong variations were observed between treatments. Following nutrient addition on day 18, a phytoplankton bloom was evident in chlorophyll a data from day 19 or 20 with chlorophyll a peaking on day 21 or later (Hopwood et al., 2018a). An increase in Fe(II) was then evident from days 20-29 under bloom and post-bloom conditions (Fig. 5 (a)).

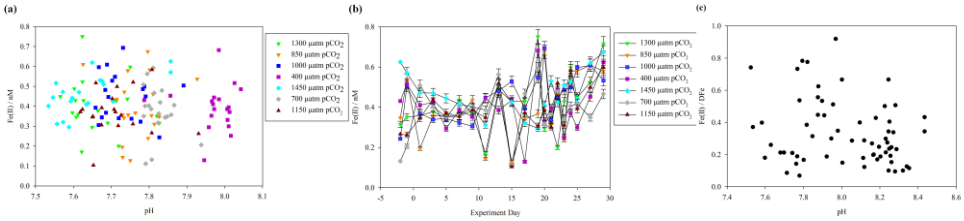


Figure 5: (a) Fe(II) concentrations (unfiltered) during the Gran Canaria mesocosm plotted against measured mesocosm pH (b) Fe(II) concentrations over the duration of the Gran Canaria mesocosm experiment. The 550 µatm pCO_2 mesocosm was discontinued after leakage and exchange with surrounding seawater occurred on experiment day 3 and so no data is shown (c) Fe(II)/DFe for all available timepoints from MesoArc and MesoPat.

Contrasting days 1 and 29, Fe(II) in all of the mesocosms except number 7 experienced a measurable increase in Fe(II) concentration (+0.4, +0.4, +0.2, +0.2, +0.2, 0.0 and +0.3 nM respectively from mesocosm number 2 to 8). Mesocosm 7 was also anomalous with respect to slow post-bloom nitrate drawdown and elevated H_2O_2 concentration (100 nM H_2O_2 greater than other treatments under post-bloom conditions (Hopwood et al., 2018a)). Overall, despite the large gradient in pCO_2 (400-1450 µatm and a corresponding measured pH range of 8.1-7.7), Fe(II) showed no significant correlation with pH (Pearson Product Moment Correlation p 0.32) (Fig. 5 (b)).

3.5 Fe(II) decay experiments (Patagonia and Svalbard)

During the Ocean Certain MesoArc and MesoPat experiments, a series of decay experiments (n = 79) was conducted to investigate the stability of in situ Fe(II) concentrations. The 79 time points at the start of these experiments were made before water was moved from ambient lighting into the dark and can be considered as in situ Fe(II) concentrations. Across the complete dataset, the properties known to affect the rate of Fe(II) oxidation in seawater varied over relatively large ranges for the various experiments; temperature 4.0-18°C, salinity 22.7-33.8, pH 7.46-8.44, 315-449 µM O_2, and 1-79 nM H_2O_2 (see Supplementary Material A). Initial Fe(II) concentrations ranged from 0.3-16 nM. Generally a decline in Fe(II) was observed immediately after transferring this sampled water to a dark box, yet this was not always the case. The Fe(II) concentration more often than not remained measurable (> 0.2 nM) for the entire duration of the decay experiment. One hour after the transfer of water from ambient conditions into the dark, Fe(II) was below detection on only 2 out of 79 occasions, and on average 55% of the initial Fe(II) concentration at t = 0 remained.

In order to account for the many physio-chemical parameters that affect Fe(II) oxidation rates, theoretical pseudo first order rate constants (k') were calculated for each decay experiment (n = 79) using measured pH, salinity and temperature as per Eq. (2) (Santana-Casiano et al., 2005) where T is temperature (°K), pH is pH_{free} and S is salinity (psu). O_2 saturation was calculated as per Garcia and Gordon (1992) and then k' was adjusted for measured O_2 concentrations as per Eq. (3). Measured rate constants (k'_{meas}) were derived from the gradient of ln[Fe(II)] against time for each decay experiment from at

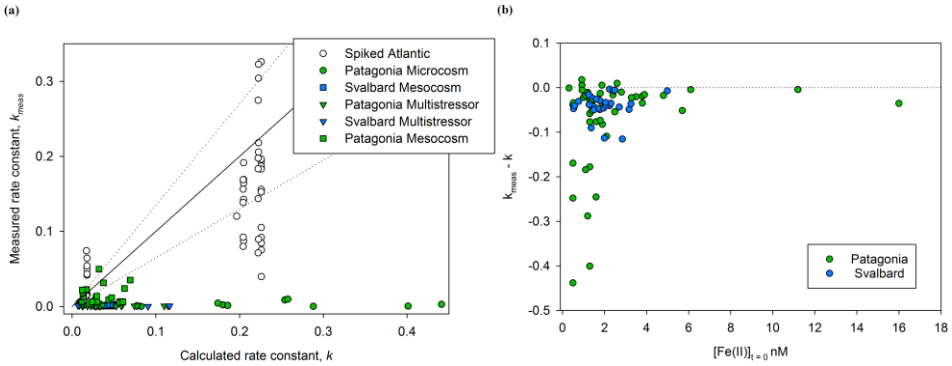
least 5 sequential datapoints (Fe(II) concentration was obtained at 2 minute intervals). One potential complication with calculating oxidation rates is that Fe(II) is oxidised via both O_2 and H_2O_2 in surface seawater (King et al., 1995; Millero and Sotolongo, 1989). Fortunately, the MesoPat and MesoArc experiments were notable for low H_2O_2 concentrations due to the enclosed HDPE containers used (Hopwood et al., 2018b) and therefore literature oxidation constants describing the oxidation of Fe(II) via O_2 derived under low H_2O_2 conditions are particularly appropriate constants to use.

Equation 2 $$log k' = 35.407 - (6.7109 \times pH_{free}) + (0.5342 \times pH_{free}^2) - \left(\frac{5362.6}{T}\right) - (0.04406 \times S^{0.5}) - (0.002847 \times S)$$

Equation 3 $$k = \frac{k'}{[O_2]}$$

The rate constant, k (Eq. 3), thus accounts for the major effect of variations between experiments of salinity, temperature, pH and O_2 in a single constant. Before comparing k_{meas} and k, an estimate of the uncertainty should also be made as differences between the two values may arise due to the relatively large combined error from propagating the uncertainty in $S/T/pH_{free}/[O_2]$, and in analytical error on Fe(II) measurements. The accuracy of Fe(II) measurements is challenging to quantify for a transient species with no appropriate reference material. In this case, the exact Fe(II) detection method used here was previously compared to another variation of the luminol chemiluminescence method (with pre concentration, Hopwood et al., 2017) and k_{meas} was determined with ±20% difference between two methods. The uncertainty on k_{meas} is therefore assumed to be ±20% rather than the generally smaller uncertainty than can be calculated from linear regression of ln[Fe(II)]. The uncertainty in calculated k can be assessed by calculating the change resulting from the estimated uncertainty on measured salinity (±0.1), temperature (±0.5°C), pH_{free} (±0.05) and O_2 (±10 µM). The combined uncertainty is ±35% for k. Reduced uncertainties are possible with closed thermostat systems where the uncertainty on all physical/chemical parameters ($S/T/pH/O_2$) would be significantly reduced, however our objective here was to measure the decay rates of in situ Fe(II) concentrations and thus the first priority was to commence measurements after sub-sampling rather than to stabilize physical/chemical conditions.

In order to further understand the cause of any systematic discrepancies in the dataset between measured k_{meas} and calculated k, an additional set of experiments was conducted using aged South Atlantic seawater. This water was previously stored in 1 m^3 trace element clean HDPE containers for in excess of 1 year and was maintained in the dark at experimental temperature for 3 days prior to commencing any experiment. The background concentration of Fe(II) in this water was below detection (<0.2 nM) and the initial DFe concentration relatively low (0.98 ± 0.39 nM). In a series of 47 decay experiments, Fe(II) spikes of 2-8 nM were added and then the decay in the dark monitored as per the Arctic/Patagonia in situ experiments.



~~**Figure 6: A comparison of k_{meas} and calculated k (both M^{-1} min^{-1}) for Fe(II) decay experiments. (a) Rate constants for Fe(II) decay experiments from Patagonia (green), Svalbard (blue) and spikes to aged Atlantic seawater (colourless) (b) The difference between observed and calculated values of k (k_{meas} - k) is shown against Fe(II) concentration at t = 0.**~~

~~Contrasting k with k_{meas} (Fig. 6), it is immediately apparent that the Fe(II) present within Arctic/Patagonia experiments was generally much more stable than would be predicted for an equivalent inorganic spike of Fe(II) added to water with the same physical/chemical properties i.e. in most cases k_{meas} < k. Three plausible hypotheses can be conceived for this offset:~~

~~i. The measured rates here refer to relatively low initial Fe(II) concentrations (0.3-16 nM) compared to the concentrations at which rate constants have been derived (typically ~20-200 nM) and the difference arises simply because the rate constants are not calibrated for low nanomolar starting concentrations.~~

~~ii. There is 'dark' production of Fe(II) in the experiments i.e. on-going formation of Fe(II) counter acts the first order decay of Fe(II) via oxidation.~~

~~iii. The speciation of Fe(II) in seawater is more stable with respect to oxidation than the species for which the rate constants are calculated.~~

~~For the series of experiments using spikes of Fe(II) in South Atlantic seawater, k_{meas} is consistently closer to k than for any in-situ experiments (Fig. 6a). Nevertheless, some datapoints for spiked South Atlantic seawater still fall outside the ±35% uncertainty boundary. As the spiked experiments closely matched the initial Fe(II) concentrations in the in-situ decay experiments, the higher Fe(II) concentrations generally used to establish the rate of Fe(II) decay in laboratory experiments cannot be the main explanation for a discrepancy between k_{meas} and k, although it may be a minor contributing factor.~~

~~Calculating the difference between calculated and measured k (Δk), it is evident that the largest differences were associated with the lowest initial Fe(II) concentrations (Fig. 6b). This is consistent with both hypothesis II and III. Assuming that the dominant source of Fe(II) is photochemistry, the effects of both a secondary 'dark' Fe(II) source and a limited fraction of~~

~~Fe(II) existing in a more stable form with respect to oxidation would be most evident at the lowest initial Fe(II) concentration. Sources of Fe(II) other than photochemistry are plausible and may include, for example, zooplankton grazing due to the reduced pH and O_2 within organisms' guts (Nuester et al., 2014; Tang et al., 2011). Mesozooplankton addition was one of the three experimental variables manipulated during the Arctic/Patagonia experiments. However, no clear trend was evident with respect to the measured offset in k and the zooplankton addition status of the experiments. Mean $\Delta k \pm SD$ ($\times 10^{-2}$) for the high/low zooplankton treatments over all experiments were 4.66 ± 5.79 and 4.08 ± 5.63, respectively. A dependency of Δk on the initial Fe(II) (Fig. 6b), with $[Fe(II)]_{t=0}$ likely very sensitive to multiple experimental factors such as the time of day that the sample was collected and the exact time delay between sample collection and the first timepoint for each Fe(II) decay experiment, would however make determining the relative importance of any other underlying causes challenging. In order to gain further insight into the potential role of zooplankton in Fe(II) release under dark conditions, a series of incubations was conducted with addition of the copepod *Calanus finmarchichus* to cultures of the diatom *Skeletonema costatum* (Hopwood et al., 2018b). No change in extracellular Fe(II) or H_2O_2 concentrations were evident across a gradient of copepods from 0-10 L^{-1}. Whilst this suggests the role of high/low zooplankton treatments was minimal in short term changes to ambient Fe(II) concentrations, the potential release of Fe(II) by zooplankton may of course be species specific; different results may have been obtained with different zooplankton-prey combinations.~~

~~**4 Discussion**~~

~~**4.1 Assessing the extent of Fe contamination within mesocosms**~~

~~Whilst both DFe and TdFe inputs into any incubation experiment can be determined, DFe does not behave conservatively, is actively taken up by microorganisms and scavenged onto particle surfaces. Thus the relationship between TdFe and DFe is not a simple linear function (Fig. 2). The equilibrium concentration of Fe within particulate and dissolved phases depends on factors such as Fe(III) ligand, or more generally DOC, concentrations (Wagener et al., 2008) and particle loading (Bonnet and Guieu, 2004; Rogan et al., 2016).~~ All of the incubation experiments herein were conducted using coastal or near-shore waters. This is reflected in the low salinities of the MesoPat (27.5-28.0) and MesoArc (33.7-33.8) mesocosms. Both of these fieldsites were fjords with high freshwater input. Comau fjord (Patagonia, MesoPat) is situated in a region with high annual rainfall and receives discharge from rivers including the River Vodudahue. Kongsfjorden (Svalbard, MesoArc) receives freshwater discharge from numerous meltwater fed streams and marine terminating glaciers in addition to melting ice. Correspondingly high DFe and TdFe concentrations were thereby found in surface waters; universally >4 nM DFe. The Gran Canaria (initial S 37.0) mesocosm cannot be considered to have had a coastal low salinity signature from large freshwater outflows, but was still conducted using near-shore waters which would generally be expected to contain higher Fe concentrations than offshore waters due to benthic sources of Fe (see, for example, Croot and Hunter, 2000). Despite the inshore basis of the MesoArc mesocosm, Fe contamination was a small, but significant, fraction of the TdFe added to the

starting water (8%, 3.6 nM~~).~~ , Fig. 1). It is not anticipated that this small TdFe addition will have had any adverse effect on the Fe redox chemistry results presented herein for the Meso/micro/multi Arc/Pat experiments.

4.2 Fe speciation within the mesocosms

Throughout all of the ~~MesoArc/MesoPat~~Meso/micro/multi Arc/Pat experiments, Fe(II) consistently constituted a large fraction of DFe (Table 4). The presence of 24-65% of DFe in mesocosms as Fe(II) is not unexpected, as the photoreduction of Fe(III) species by sunlight is well characterized (Barbeau, 2006; Wells et al., 1991). Yet it also raises questions about how Fe speciation is modelled in these waters. DFe in the ocean is ~~almost universally~~widely assumed to be characterised as "99% complexed by organic species"(Gledhill and Buck, 2012) on the basis of extensive research using voltammetric titrations to determine the strength and concentration of Fe binding ligands (Van Den Berg, 1995; Rue and Bruland, 1995). Yet these approaches exclusively measure Fe(III)-L species (Gledhill and Buck, 2012).

Dataset	f [Fe(II)]/[DFe]	f [DFe]/[TdFe]	n
MesoArc ~~mesocosm~~	0.30 ± 0.14	0.15 ± 0.06	20
~~MesoArc multistressor~~MultiArc	0.30 ± 0.17	0.07 ± 0.01	8
Svalbard, ambient (light)	0.11 ± 0.05	<0.01	5
~~MesoPat microcosm~~MicroPat	0.24 ± 0.14	0.76 ± 0.34	10
MesoPat ~~mesocosm~~	0.65 ± 0.52	0.20 ± 0.17	22
~~MesoPat multistressor~~MultiPat	0.47 ± 0.44	0.35 ± 0.30	15
Patagonia, ambient (light)	0.06 ± 0.04	0.12 ± 0.01	5
Patagonia, ambient (dark)	0.02 ± 0.00	0.15 ± 0.11	3

Table 4. Fraction of dissolved Fe concentration ([DFe]) present as Fe(II), and fraction of total dissolvable Fe concentration ([TdFe]) present as DFe. n, number of datapoints. *ND*, not determined. All values are mean ± standard deviation.

Here we should note that the method utilized during these incubation and diurnal experiments, flow injection analysis with a PTFE line inserted directly into the experiment water, is relatively well suited for establishing the in-situ concentration of Fe(II) (O'Sullivan et al., 1991). Such an experimental set up ensures no unnecessary delay is introduced between the collection and analysis of a sample. When using an opaque sampler, such as a Go-Flo bottle typically deployed at sea for collection of trace element samples (Cutter and Bruland, 2012), the collection process inevitably displaces near-surface water from its ambient light conditions for a time period that constitutes >1 half-life of Fe(II) in warm, oxic seawater. Measured near-surface Fe(II) concentrations on samples from a rosette system would therefore always be expected to under-estimate in-situ Fe(II) concentrations (O'Sullivan et al., 1991).

Fe(II) concentration was also quantified in ambient waters adjacent to the mesocosms and found to constitute a lower fraction of DFe (2-11%). Most of the decay experiments, from which initial Fe(II) concentrations are reported ~~in~~ (Table 4~~,~~), were conducted at the end of mesocosm/microcosm/multistressor experiments and thus it is not possible to assess the development of Fe(II) stability throughout ~~the~~a phytoplankton bloom~~ in the Patagonia or Svalbard experiments~~. Nevertheless, the high fraction of DFe present as Fe(II) in these experiments (Table 4) relative to that observed in ambient waters is consistent with the increase in Fe(II) concentrations observed in Gran Canaria after the initiation of the phytoplankton bloom (day 19 onwards, Fig. ~~5 (b)).~~3b). The ~~Patagonia/Svalbard~~Meso/micro/multi Arc/Pat experiments had macronutrient additions daily, whereas the Gran Canaria experiment had macronutrient addition only on day 18. The conditions within the ~~Arctic/Patagonia~~Meso/micro/multi Arc/Pat experiments during the time period which decay experiments were conducted were therefore typical of those during, or shortly after, a phytoplankton bloom. Whilst chlorophyll a was not quantified for ambient waters, for which Fe(II) data are reported ~~in~~ (Table 4~~,~~), sampling in Svalbard (MesoArc, July 2015) and Patagonia (MesoPat, November 2014) ~~occured~~occurred during relatively low productivity phases relative to the annual cycle in primary production at these fieldsites (Hop et al., 2002; Iriarte et al., 2013). The ambient concentrations of Fe(II) measured at the mesocosm experiment fieldsites are therefore not necessarily directly comparable to Fe(II) concentrations measured after nutrient addition in the corresponding mesocosm experiments.

4.3 Fe(II) decay experiments

~~Fe(II) oxidation rates are relatively well constrained in seawater with varying temperature, salinity, pH, H_2O_2 and O_2 concentration from extensive series of experiments where the change in concentration of an Fe(II) spike was monitored with time and the rate constants for oxidation with O_2 and H_2O_2 then derived from first order kinetics (e.g. King et al., 1995; Millero et al., 1987b). Whilst dissolved O_2 is the dominant oxidizing agent for Fe(II), H_2O_2 is also of importance as an Fe(II) oxidizing agent in surface seawater (González-Davila et al., 2005; King and Farlow, 2000; Millero and Sotolongo, 1989). The unusually low concentration of H_2O_2 within the Patagonia and Svalbard experiments due to the enclosed HDPE mesocosm design and/or synthetic lighting (Hopwood et al., 2018b) was therefore fortunate from a mechanistic perspective as it allows the simplification that O_2 was the only major oxidising agent. The much lower H_2O_2 concentrations (1-79 nM)~~

~~present, compared to ambient surface waters, during the Patagonia and Svalbard experiments should mean that Fe(II) decay rates during these experiments more closely match the oxidation rate constants used to derive Eq. 2 (which were derived for low-H_2O_2 conditions).~~

~~The decay experiments reported here still however differ in two critical respects from controlled oxidation rate experiments used to derive rate constants. First, the speciation of Fe(II) may differ.~~ Fe(II) oxidation rates are relatively well constrained in seawater with varying temperature, salinity, pH, H_2O_2 and O_2 concentration from extensive series of experiments where the change in concentration of an Fe(II) spike was monitored with time and the rate constants for oxidation with O_2 and H_2O_2 then derived from first order kinetics (King et al., 1995; Millero et al., 1987). Whilst dissolved O_2 is the dominant oxidizing agent for Fe(II), H_2O_2 is also of importance as an Fe(II) oxidizing agent in surface seawater (Millero and Sotolongo, 1989; King and Farlow, 2000; González-Davila et al., 2005). The unusually low concentration of H_2O_2 within the Meso/micro/multi Arc/Pat experiments due to the enclosed HDPE mesocosm design and/or synthetic lighting (Hopwood et al., 2018a) was therefore fortunate from a mechanistic perspective as it allows the simplification that O_2 was the only major oxidising agent. The much lower H_2O_2 concentrations (1-79 nM) present, compared to ambient surface waters, throughout the Meso/micro/multi Arc/Pat experiments should mean that Fe(II) decay rates during these experiments more closely match the oxidation rate constants used to derive Eq. 1 (which were derived for low-H_2O_2 conditions).

The decay experiments reported here still however differ in two critical respects from controlled oxidation rate experiments used to derive rate constants. First, the speciation of Fe(II) may differ. It is debatable to what extent Fe(II)-L species, analogous to Fe(III)-L species, exist in surface marine waters due to the absence of reliable techniques to probe Fe(II)-organic speciation (Statham et al., 2012)~~, but~~. Yet there is consistent evidence that organic material affects Fe(II) oxidation rates (see below). Second, these decay experiments measure the change in Fe(II) concentration between light and dark conditions and not specifically the oxidation rate. If photochemical Fe(II) production was the sole Fe(II) source, and oxidation of Fe(II) via H_2O_2 and O_2 were the only Fe(II) sinks, then the decay rate measured here would approximate the oxidation rate determined under controlled laboratory conditions. However, there are possible biological sources of Fe(II) ~~(Nuester et al., 2014; Sato et al., 2007)~~(Sato et al., 2007; Nuester et al., 2014), the possibility of biological uptake of Fe(II) (Shaked and Lis, 2012) and cross-reactivity with other reactive trace species (e.g. ~~reactive oxygen species and Cu, Croot and Heller, 2012) to consider. All of~~reactive oxygen species and Cu, Rijkenberg et al., 2006, Croot and Heller, 2012) to consider. These complexities make Fe(II) more challenging to model in natural waters compared to controlled conditions. This is especially the case at the low Fe(II) concentrations relevant to the surface ocean where Fe(II) concentrations range from below detection up to ~1 nM (Gledhill and Van Den Berg, 1995; Hansard et al., 2009; Sarthou et al., 2011).

Contrasting k with k_{meas} during Fe(II) decay experiments (Fig. 4), it is immediately apparent that the Fe(II) present within Meso/Micro/Multi Arc/Pat experiments was generally much more stable than would be predicted for an equivalent

inorganic spike of Fe(II) added to water with the same physical/chemical properties i.e. in most cases $k_{meas} < k$. Three plausible hypotheses can be conceived for the offset:

i. The measured rates here refer to relatively low initial Fe(II) concentrations (0.3-16 nM) compared to the concentrations at which rate constants have been derived (typically ~20-200 nM) and the difference arises simply because the rate constants are not calibrated for low nanomolar starting concentrations.

ii. There is 'dark' production of Fe(II) in the experiments i.e. on-going formation of Fe(II) counter-acts the first order decay of Fe(II) via oxidation.

iii. The speciation of Fe(II) in seawater is more stable with respect to oxidation than the species for which the rate constants are calculated.

For the series of experiments using spikes of Fe(II) in Atlantic seawater, k_{meas} is consistently closer to k than for any in-situ experiments (Fig. 4a). Nevertheless, some datapoints for spiked Atlantic seawater still fall outside the ±35% uncertainty boundary. As the spiked experiments closely matched the initial Fe(II) concentrations in the in-situ decay experiments, the higher Fe(II) concentrations generally used to establish the rate of Fe(II) decay in laboratory experiments cannot be the main explanation for a discrepancy between k_{meas} and k. Furthermore, differences in the formulation of k' between studies are relatively minor (Millero et al., 1987; King et al., 1995; Santana-Casiano et al., 2005). .

Calculating the difference between calculated and measured k (Δk), it is evident that the largest differences were associated with the lowest initial Fe(II) concentrations (Fig. 4b). This is consistent with both hypothesis II and III. Assuming that the dominant source of Fe(II) is photochemistry, the effects of both a secondary 'dark' Fe(II) source and a limited fraction of Fe(II) existing in a more stable form with respect to oxidation would be most evident at the lowest initial Fe(II) concentration. Sources of Fe(II) other than photochemistry are plausible and may include, for example, zooplankton grazing due to the reduced pH and O_2 within organisms' guts (Tang et al., 2011; Nuester et al., 2014). Mesozooplankton addition was one of the three experimental variables manipulated during the Arctic/Patagonia experiments. However, no clear trend was evident with respect to Δk and the zooplankton addition status of the experiments. Mean Δk ± SD ($\times 10^{-2}$) for the high/low zooplankton treatments over all experiments were 4.66 ± 5.79 and 4.08 ± 5.63, respectively. A dependency of Δk on the initial Fe(II) concentration (Fig. 4b), with $[Fe(II)]_{t=0}$ likely very sensitive to multiple experimental factors such as the time of day that the sample was collected and the exact time delay between sample collection and the first timepoint for each Fe(II) decay experiment, would however make determining the relative importance of any other underlying causes challenging. In order to gain further insight into the potential role of zooplankton in Fe(II) release under dark conditions, a series of incubations was conducted with addition of the copepod *Calanus finmarchichus* to cultures of the diatom *Skeletonema costatum* (Hopwood et al., 2018a). No change in extracellular Fe(II) or H_2O_2 concentrations were evident across a gradient of copepods from 0-10 L^{-1}. Whilst this suggests the role of high/low zooplankton treatments was minimal

in short-term changes to ambient Fe(II) concentrations, the potential release of Fe(II) by zooplankton may of course be species specific; different results may have been obtained with different zooplankton-prey combinations.

The high magnitude of Δk in some cases at low initial Fe(II) concentrations (Fig. ~~6~~4) is consistent with the theory that Fe(II) binding ligands are responsible for the observed stability of Fe(II) in some natural waters (Roy and Wells, 2011; Statham et al., 2012). The Fe(II)-binding capacity of any ligands present in a specific sample would be expected to become saturated as Fe(II) concentrations increased. The effect of Fe(II) ligands on the oxidation rate of an added Fe(II) spike would therefore become less evident as Fe(II) concentration increased because the fraction of Fe(II) present as Fe(II)-L species would decline i.e. ~~k_{meas}~~Δk would ~~converge with k~~approach zero. This has an important methodological implication. The effect of cellular exudates, or natural organic material extracts, on Fe(II) oxidation rate is more often than not tested by adding reasonably high nanomolar Fe(II) spikes to solution and then following the Fe(II) decay with time (see, for example, Lee et al., 2017). By raising the initial Fe(II) concentration, such an approach may however systematically under-estimate the effect of organic material on Fe(II) stability at in-situ Fe(II) concentrations.

The effect of organic material on Fe(II) is difficult to generalize as organic compounds can accelerate, retard or have no apparent effect on Fe(II) oxidation rates via oxygen (Santana-Casiano et al., 2000). However, there are now sufficient studies of Fe(II) behaviour to distinguish between the broad effects of allochthonous and autochthonous material. ~~Extracts from the green algae *Dunaliella tertiolecta* (Gonzalez et al., 2014)~~Extracts from the green algae *Dunaliella tertiolecta* (González et al., 2014), cyanobacteria *Synechococcus* (Samperio-Ramos et al., 2018b) and *Microcystis aeruginosa* (Lee et al., 2017), coccolithophore *Emiliania huxleyi* (Samperio-Ramos et al., 2018a), and diatoms *Chaetoceros radicans* (Lee et al., 2017) and *Phaeodactylum tricornutum* (Santana-Casiano et al., 2014) have all been found to retard Fe(II) oxidation rates. Furthermore, the effect of cellular exudates on the reaction constant appears to scale with increasing total organic carbon (Samperio-Ramos et al., 2018b). ~~This is also consistent with the release of Fe(II) binding agents resulting in the formation of Fe(II) L species with slower oxidation rates than inorganic Fe(II) speciation under specified physical/chemical conditions.~~ In contrast to the stabilization apparent in some cellular exudates, allochthonous material generally, although not universally, has the opposite effect with an acceleration of Fe(II) oxidation rates reported both in coastal environments (Lee et al., 2017) and using terrestrially derived organic leachates (Rose and Waite, 2003). The generally positive effects of cellular exudates on Fe(II) stability with respect to oxidation determined in single-species studies is consistent with the stability of Fe(II) observed in almost all experiments here (Fig. ~~6~~4) and this suggests that microbial cellular exudates are indeed a stabilizing influence on Fe(II) concentrations at a broad scale in ~~surface~~coastal marine environments. Stabilization of Fe(II) by freshly produced exudates could explain the sustained increase in Fe(II) concentrations across all pCO_2 treatments under post-bloom conditions in Gran Canaria (Fig. 3b) and the high fraction of DFe present as Fe(II) during all ~~Arctic/Patagonia~~Meso/micro/multi Arc/Pat experiments. (Table 4).

Apart from the influence of organic Fe(II) ligands on Fe(II) stability arising from the slower oxidation rates of some organically complexed Fe(II) species, Fe(II) binding organics may also have a role in the generation of superoxide (O_2^-) which is speculated to be a dominant mechanism for the formation of Fe(II) in the dark (Rose, 2012). Experiments with 65-130 nM of protoporphyrin IX demonstrated increased formation of Fe(II) in the dark with both increasing porphyrin concentration and increasing irradiation of seawater prior to the onset of darkness (Rijkenberg et al., 2006). Whilst the rates of this process are challenging to investigate at the sub-nanomolar porphyrin and Fe(II) concentrations expected in the ocean's dark interior, the dark formation of Fe(II) mediated by ROS interactions with Fe(II)-organic complexes could potentially be important in both the diurnal cycling of Fe in the surface ocean and the non-photochemical formation of Fe(II) in the dark of the ocean's interior (Rose, 2012). From a mechanistic perspective, it is challenging to establish definitively from the experiments herein whether apparent Fe(II) stability arises from reduced oxidation rates due to Fe(II) complexation, or dark Fe(II) formation via a mechanism, such as that proposed for superoxide, which involves Fe(II)-organic complexes. Both hypothesis are consistent with field observations and it is also possible that both processes operate in parallel.

4.4 Conclusions

The existence of a high fraction (24-65%) of DFe as Fe(II) during mesocosm experiments, and the apparent stability of low concentrations of Fe(II) ~~in these productive waters~~ suggests that the classic characterisation of '99% of dissolved Fe existing as Fe(III)-L complexes' (Gledhill and Buck, 2012) is inadequate to describe DFe speciation in ~~marine~~coastal surface waters. Fe(III)-ligand complexes may overwhelmingly dominate Fe speciation in the ocean as a whole, but in ~~sunlit surface~~coastal waters a dynamic redox cycle operates maintaining considerable concentrations of Fe(II) in solution. The stabilizing effects on Fe(II) with respect to oxidation reported here were strongest at low (<2 nM) Fe(II) concentrations suggesting that the Fe(II) stabilization mechanism is caused by a process akin to complexation where the magnitude of the effect is capped by a factor other than physical conditions.

Exudates stabilizing Fe(II) may be a poorly characterized component of the aptly named 'ferrous wheel' (Kirchman, 1996; Strzepek et al., 2005) and contribute to the efficient recycling of DFe within marine surface waters. Irrespective of whether Fe(II) is more or less bioavailable relative to Fe(III), the formation of Fe(II) is a mechanism for increasing DFe and thus increasing DFe availability to biota. Mechanisms such as the stabilization of Fe(II) by cellular exudates during and after phytoplankton blooms may therefore facilitate DFe uptake to a greater extent than would be possible in the absence of Fe-redox cycling. Both Fe(III) and Fe(II) speciation and concentration must therefore be defined in order to understand the role of Fe as a driver of marine primary production.

4 Author Contributions

All authors contributed to the design of the study and the interpretation of data. MH, CS, JG, NS, ØL and TT conducted analytical work. MH coordinated the writing of the manuscript with input from other authors.

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