We provide our responses (Plain text with blue and red colors) to all comments (*italic text*) below.

# - Response to Reviewer Comments -

**Reviewer #1**

**-General Comments:**

**1** *The abstract does not include any summary of the main conclusions that the authors have drawn from their synthesis.*

☞ We have modified Abstract (from line 21, page 1 to line 1, page 2).

**2** *It is not clear to me what the purpose of the entire Section 2.1 is. Ostensibly, the authors attempt to describe the objectives of each experiment, but I'm not convinced that this information is really important enough to merit a 2-page section, nor am I convinced that the authors explain these objectives terribly clearly. The section mixes general introduction to each experiment (e.g. descriptions of the oceanographic conditions of each site) with usually only a vague, general statement of purpose for the experiments (e.g. "To investigate the unexpected responses revealed in IronEx-1, a second OIF was conducted", or "To measure biologically-driven gas fluxes"). For some experiments, the authors only list briefly the main conclusions, but don't explain much about the objectives and design.*

☞ Thank you for pointing out this deficiency. We have revised Section 2.1 to clearly explain objectives and hypotheses of the previous artificial OIF experiments (from line 28, page 4 to line 28, page 6). We have also removed the main results from previous OIF experiments in Section 2.1.

**3** *Section 2.2 is basically a long list of measurements of initial conditions for the various experiments. Many of these have been reviewed previously, and the authors don't draw any conclusions from this 1.5-page-long section. The authors have done an excellent job of summarising this information in their tables (which I think is very useful). But since the main message seems to be that OIF have been conducted under a diverse range of initial conditions, wouldn't it be better if the authors just made that point in, maybe, 1–2 paragraphs, and then focused on advancing an argument and drawing conclusions?*

☞ Reviewer is correct. We have revised Section 2.2 (from line 30, page 6 to line 24, page 8) to explain why/how initial environmental conditions were different in each experiment. Initial environmental conditions (e.g., silicate concentration and zooplankton abundance) were determined to test hypotheses and to achieve objectives for each artificial OIF experiment and were related to biogeochemical responses after iron additions. We overall reorganized Section 2.2, and added the conclusions derived from Section 2.2 to Section 2.5 (lines 1–15, page 15).

4 *The subject matter of Section 2.3 is an important one: how many additions of iron should be made, and how should the fertilised patch be traced? What I miss in this section is to see the authors actually draw conclusions from these results. For example, are multiple additions the right way to design an experiment? At what intervals should they be made? The experiments listed vary a lot in duration, so simply listing the total number of additions, rather than the intervals at which they were made, seems uninformative. Likewise, it might be useful to see some discussion of the amount of iron added per square kilometre of patch– I believe that the additions for the various experiments varied a lot also on a per-area basis, but this is not discussed. Can we determine an optimum rate of application from the various experiments? If not, is this something that warrants further experimental work, and if so, of what kind? Likewise, the discussion of tracing methods just boils down to listing the fact that SF6 and buoys can be used, without drawing conclusions that could be formulated as practical recommendations. For example, drifting buoys in previous experiments were found to ultimately leave the patch, I believe due to wind forcing, and one of the recommendations of this paper is that experiments should be conducted that last upwards of 30 days, under which conditions multiple SF6 injections might become more necessary.*

☛ Good point. We have substantially revised Section 2.3 Iron addition and tracing methods by describing how previous OIF experiments injected iron and traced fertilized patches, why most previous OIF experiment conducted multiple iron addition, and pros and cons of tracing methods (from line 26, page 8 to line 6, page 10). We have also added the conclusions derived from Section 2.3 to Section 2.5 (lines 16–25, page 15). In Section 4 Future: Designing future aOIF experiments, we have added discussion/suggestion about intervals of iron addition and the amount of iron added per $km^2$ of patch, tracing method to maximize the effectiveness of OIF experiments based on Section 2.3 (line 33, page 24 to line 38, page 25).

5 *Section 2.4 I think mostly re-hashes just the main findings of previous experiments, and again does so in an often rather long-winded way (e.g. the information about spatial pattern of the SOFEX blooms doesn't seem to contribute much). All in all, this section does not really build up an integrated understanding of the biogeochemical responses to iron addition, but reads rather more like a selective catalogue of results picked rather haphazardly from the different experiments: e.g. the difference in maximum chlorophyll between SEEDS-I and SEEDS-II is pointed out, but this isn't part of a broader discussion of chlorophyll levels across the different OIF and what their causes might be. In the next paragraph, SEEDS-I and EIFEX are compared with max chl-a concentration and integrated chl-a stock, but this is not compared with other experiments. My point here is not to ask the authors to add specifically a discussion of chlorophyll, I am just pointing this out as an instance of where the paper rather shies away from reaching interesting new insights. The entire section then simply ends, without any attempt to conclude anything from all this information, aside from pointing out in the middle of the penultimate paragraph that integrated primary production ought to be monitored in future experiments.*

☞ Thank you for your comment. We have substantially revised Section 2.4 Biogeochemical responses (from line 8, page 10 to line 37, page 14). To reflect the Reviewer's suggest, we have added the integrated conclusion derived from Section 2.4 to Section 2.5 (from line 22, page 15 to line 25, page 16). For your information, three conditions, at least, are inevitable to detect significant carbon export to deep waters following increase in PP as follows: (1) a shift to a diatom-dominated community, (2) low bacterial respiration and grazing pressure rates within the mixed layer, and (3) a sufficient experimental duration, enabling both immediate and delayed responses to iron addition to be observed.

**6** *I had previously requested that the authors make explicit definitions of terms like "efficiency" and "sequestration" in the context of carbon fluxes, but these terms are still used loosely without specific definitions. I think this is a significant problem when discussing the planning of future iron fertilisation work, as it is critical to achieving the stated objectives to ensure that the correct measurements are made, and this can only be done if we define clearly what we need to measure. I would suggest that the authors refer to the Lampitt et al. paper in the 2008 special issue of the Philosophical Transactions (same issue as the cited Smetacek & Naqvi paper), titled "Ocean fertilization: a potential means of geoengineering?". This paper discusses explicit definitions of terms such as carbon sequestration with reference to the depth of winter mixing, and discusses how they can be measured.*

☞ We apologize this confusing. To exactly explain definition about "sequestration" (i.e., organic carbon flux exported from the mixed layer into intermediate/deep waters) in Section 1 introduction, we have cited Lampitt et al. (2008) and have added new Figure 3c (page 57). We have also added a sentence to define the effectiveness of artificial OIF as follows:

- 1. Introduction (from line 40, page 3 to line 2, page 4):

"However, for aOIF to be considered as a useful geoengineering approach (IPCC, 2007), in the long run, the most critical issue is whether the substantial amounts of organic carbon produced by aOIF in the surface waters lead to a significant export to intermediate/deep layers and long-term (~1,000 years) storage (Fig. 3c) (Lampitt et al., 2008)."

**7** *Section 2.5 again leaves me rather unsatisfied: the authors present a list of findings, but don't make any argument or properly discuss reasons for the divergent outcomes. As a result, by the end of the section, it is not clear to the reader why "the effectiveness of iron addition on this component of the biological pump remains a question". In other words, the authors should be using this section to discuss why the previous 13 experiments have not managed to yield clear answers to the effectiveness of carbon sequestration. The answer lies in a combination of experiment duration, measurement methods (measuring only shallow or also deeper fluxes), patch size (with a very small patch, I suspect that deeper traps might miss export that may be occurring because the plume of sinking particles is confined to such a small area), and patch movement (tracking deep export is easy in a stationary patch, but very hard in a large patch). Although the authors do draw these conclusions in a very general sense, saying at* *the end that future experiments need to last long enough, fertilise a largeish area, and use multiple methods, the justification of publishing a review paper like this one must lie in a more detailed analysis of how which of the previous OIF were unable to achieve these requirements. To do this, the authors would need to delve more into the details of each experiment, rather than spending most of the time reviewing the basic biogeochemical responses of each experiment. Again, terms like "effectiveness of iron addition" could be defined in very specific ways, and using language as loosely as this does not help with achieving insights.*

☞ We agree to the Reviewer's comment. More discussion is necessary. We have moved this Section to 2.4 Biogeochemical responses to describe the results of export fluxes after iron additions as follows:

- 2.4.1. Equatorial Pacific (lines 12–22, page 11):

"To determine whether the biological pump (i.e., export production) is enhanced after iron addition, the export flux of particulate organic carbon (POC) can be estimated using, individually or in combination, chemical tracers such as the natural radiotracer thorium-234 ($^{234}$Th; half-life = 24.1 days) and the stable carbon isotope of particulate organic matter ($\delta^{13}C_{org}$), sediment traps, transmissometers, and underwater video profilers (UVPs) (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). The $^{234}$Th radionuclide has a strong affinity for particles, and the extent of $^{234}$Th removal in the water column is indicative of the export of POC associated with surface PP out of the mixed layer (Buesseler, 1998). IronEx-2 was the first aOIF experiment in which the POC flux was estimated (Bidigare et al., 1999). The $^{234}$Th deficiency from the surface to 25 m was measured in the iron-fertilized patch to estimate iron-stimulated export production in the surface layer (Table 5). However, no $^{234}$Th measurements were made in the unfertilized patch for comparison, and no measurements in the deep ocean were undertaken to demonstrate deep carbon export (Bidigare et al., 1999)."

- 2.4.2. Southern Ocean (from line 38, page 12 to line 25, page 13):

"SOIREE was the first aOIF experiment in the SO to estimate the downward carbon flux into deep waters (Fig. 3c). They used a comprehensive suite of methods such as the deployment of a drifting trap, $^{234}$Th and $\delta^{13}C_{org}$ estimates derived from high-volume pump sampling, and a beam transmissometer (Nodder and Waite, 2001). However, no measurable change in carbon export was observed in response to iron-stimulated PP (Table 5 and Fig. 8b) (Charette and Buesseler, 2000; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001). During EisenEx, an increased downward carbon flux estimated from $^{234}$Th deficiency was observed in the iron-fertilized patch as the experiment progressed. However, there were no clear differences between in- and outside-patch carbon fluxes (Buesseler et al., 2005). During SOFeX-S, significantly enhanced POC fluxes below the mixed layer after iron enrichment were obtained from $^{234}$Th observations (Buesseler et al., 2005). However, the absolute magnitude of these flux increases was similar to that observed in natural blooms. Uniquely, SOFeX-N used only free-profiling robotic Lagrangian carbon explorers equipped with transmissometers to estimate the downward carbon flux without employing chemical tracers, and observed large POC flux events between day ~27 and ~45 after the first iron addition (Bishop et al., 2004; Coale et al., 2004). However, it was unclear whether surface-fixed carbon was well and truly delivered into intermediate/deep depths. For SAGE and LOHAFEX experiments, which were conducted under silicate limited conditions (Table 3, Figs. 4c and 6f), there was no detection of fertilization-induced export by any method (Table 5) (Peloquin et al., 2011; Martin et al., 2013). This result was likely to be associated with the pico-plankton dominated community, which led to rapid recycling in the mixed layer and less downward carbon flux. In contrast to the other aOIF experiments, EIFEX, which was conducted within the core of an eddy, provided clear evidence of carbon export stimulated by artificial iron addition (Jacquet et al., 2008; Smetacek et al., 2012). During EIFEX, the initial export flux, estimated from $^{234}$Th in the upper 100 m of the fertilized patch, was ~340 mg C m$^{-2}$ d$^{-1}$ (Table 5 and Fig. 8a) (Smetacek et al., 2012). This value remained constant for about 24 days after iron addition. Between day 28 and 32 a massive increase in carbon export flux (maximum of ~1692 mg C m$^{-2}$ d$^{-1}$) was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Table 5 and Fig. 8a). The profiling transmissometer with high-resolution coverage confirmed this result, showing an increase in exported POC below 200 m after day 24. At least half the iron-induced biomass sank (via the formation of aggregates of diatom species, in particular '*Chaetoceros dichaeta*') to a depth of 1,000 m, with a tenfold higher sinking rate (500 m d$^{-1}$), compared to the initial conditions (Smetacek et al., 2012). Significant changes in export production were not found in any of the other aOIF experiments and, therefore, the impact of artificial iron addition on this component of the biological pump needs to be resolved in future OIF experiments (Boyd et al., 2004; Smetacek et al., 2012; Martin et al., 2013)."

- 2.4.3. Subarctic North Pacific (lines 27–33, page 14):

"Despite the formation of a massive iron-induced phytoplankton bloom during SEEDS-1, there was no large POC export flux during the observation period (Table 5) (Tsuda et al., 2003; Aono et al., 2005; Aramaki et al., 2009). During SERIES and SEEDS-2, which allowed comprehensive time-series measurements of the development and decline of the iron-stimulated bloom, POC fluxes estimated by the drifting traps in the fertilized patch displayed temporal variations (Boyd et al., 2004; Aramaki et al., 2009). However, the results suggested that only a small part of the decrease in the mixed layer POC was subsequently captured by the drifting trap, and POC flux losses were mainly governed by bacterial remineralization and mesozooplankton grazing (Boyd et al., 2004; Tsuda et al., 2007)."

☞ We have added the discussion about the effectiveness of carbon sequestration influenced by experiment design and experiment condition (i.e., initial silicate concentrations, diatom bloom, grazing pressure, bacterial respiration, and experiment duration described in Section 2 Past: Overview of previous aOIF experiments to Section 2.5 Significant results in previous OIF experiments (lines 4–25, page 16). Also, to discuss/suggest which of export flux measurement methods can be optimal to exactly track and quantify carbon export flux, we have created new Section 3.1 Export flux measurement methods (from line 9, page 17 to line 36, page 18).

**8** *Section 2.6 starts as a promising paragraph (in fact, I think this could be a good introductory paragraph to the entire Section 2), but then falls flat for the same reasons pointed out above. What are we to conclude from these diverse outcomes? Which experiments may have missed an export event, or deep fluxes of sinking particles, and* *for what reasons? The issue of ecosystem responses and grazing is clearly an important one, but receives hardly any discussion.*

☞ We have moved the first paragraph in Section 2.6 to the introductory paragraph for Section 2 Past: Overview of previous aOIF experiments (lines 17–26, page 4). Revised Section 2.5 Summary of the significant results from aOIF experiments (from line 1, page 15 to line 25, page 16) may answer to the questions on "what are we to conclude from these diverse outcomes?, which experiments may have missed an export event?, and for what reasons?". In addition, please refer Responses of 3–5 and 7.

**9** *After all this extensive review of previous OIF in Section 2, the review suddenly moves on to possible side-effects. What conclusions can be drawn from all of the data that the authors have reviewed in Section 2?*

☞ Thank you for comment. We have revised Section 2.5 Summary of the significant results from aOIF experiments (from line 1, page 15 to line 25, page 16) to draw the conclusions reviewed in Section 2 Past: Overview of previous aOIF experiments.

**10** *Section 3.1 is slightly better, as it at least ends with a proper attempt at conclusions. However, the section is again mostly a cataloguing of results from previous experiments. What would be more useful is if the authors attempted to synthesise the insights and discussions of the publications about the individual studies so that we can at try and find patterns in the large variability between studies.*

☞ Thank you. We have moved/revised this Section to Section 3.2 Considering environmental side effects (from line 37, page 18 to line 27, page 21). We have classified possible side effects into climate-relevant gases emission (i.e., $CH_4$, $N_2O$, dimethylsulfide, and halogenated volatile organic compounds) that is produced by biological activities and/or photochemical reactions before and after iron additions, and decrease in dissolved oxygen and increase in domoic acid that lead to the changes in the ocean ecosystem following OIF. Finally, we suggested that monitoring of the productions of climate-relevant gases and domoic acid is essential to evaluate the effectiveness of OIF as a geoengineering approach, as they may directly modify the desired carbon sequestration effectiveness and can do so both positively and negatively.

**11** *Section 3.2 implies a discussion of the international legal situation, but the first paragraph is not about legal matters at all. The second paragraph does a decent job of summarising the legal situation. However, since the London Convention explicitly grants exemption only to scientific experiments in "coastal waters" I wonder where that would leave open-ocean experiments in practice. Of course, iron fertilising coastal waters is pointless, as everyone in the oceanographic community knows, but are the authors confident that legitimate research projects in the open ocean will get approval? Some clarification of this seems called for here, at least to the best of the* *authors' ability.*

☞ We apologize for the confusion. Based on the Reviewer's comments, we have removed the first paragraph. We have also moved this Section to Section 3.3 Regulation of aOIF: International law of the sea as it applies to aOIF and have revised Section 3.3 to clarify the legal situation for artificial OIF experiment in the open ocean (from line 29, page 21 to line 24, page 22).

**12** *Section 4 finally attempts to put forward some practical suggestions. However, I think that this needs to be expanded on and made more specific. Simply concluding that "multiple additions of iron are more efficient" is not the same as formulating specific guidelines about fertilisation levels (e.g. minimum addition per km2) and application intervals. Likewise, the third paragraph in this section ("What") is much too brief a discussion to be genuinely useful and to move the field forward. A long list of measurements is put forward without discussion of the relative merits of each, or a real discussion of the difficulty of tracking a fertilised patch, and whether we've learnt how to do this better over the 13 experiments that have been conducted. Likewise, the discussion of how to measure carbon fluxes is too indiscriminate a list to be of much use. What would really help would be an evaluation of what the various measurements contribute to our understanding, what their pitfalls are (especially, for example, surface-tethered sediment traps, which are probably better avoided in favour of their neutrally buoyant counterparts), and, again, where in the water column we really need to be measuring. The fact that the sections concludes in saying that carbon fluxes need to be monitored using "both trap fluxes and/or 234Th deficiency" is somewhat worrying: surely, one of the lessons from previous experiments is that both measurements really are needed, and that traps must be at multiple depths so that we can track both the export out of the surface as well as the sequestration below the depth of winter mixing? In discussing possible candidate regions, it would be useful if the authors proposed specific regions, rather than just making general observations such as recommending "regions with high silicate concentrations and low copepod abundances".*

☞ Thank you for comments. We have modified Section 4 Future: Designing future aOIF experiments (from line 26, page 22 to line 31, page 26) to put forward some practical suggestions for location (i.e., 'Where'), timing (i.e., 'When'), duration (i.e., 'How long'), modes of iron addition (i.e., 'How'), tracking methods/parameters measurements/protocols (i.e., 'What'), and side effects on marine/ocean ecosystems (i.e., 'What concern') including discussion of "fertilization levels (e.g. minimum addition per $km^2$), application intervals, the difficulty of tracking a fertilized patch, how to measure carbon fluxes, and possible candidate regions" to maximize the effectiveness of OIF experiments in the future based on the descriptions of Sections 2 and 3.

**13** *The manuscript ends with the design proposal for KIFES. Even though KIFES currently has no funding, it is an experiment that the authors clearly hope to conduct in more or less this form in the future. Therefore, I think it is valuable to have this section in the manuscript. What might be useful is if the authors used this opportunity to explain in slightly more detail how the design of KIFES will avoid the problems encountered in earlier experiments,* *i.e. explain the specifics of duration, patch size, measurement methods, etc.*

☛ Thank you for pointing this out. To reflect the Reviewer's suggestion, we have revised Section 5 Design of the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES). Based on previous artificial OIF experiments, in Section 5.1 Background - Bransfield Basin (from line 34, page 26 to line 36, page 27), we have set up the purposes of KIFES; (1) implementation of a scientific artificial OIF experiment complying with "Assessment Framework for Scientific Research Involving Ocean Fertilization" for the first time after assessment framework was accepted from LC/LP in 2010 (Resolution LC-LP.2, 2010), (2) evaluation the effectiveness of scientific artificial OIF in terms of atmospheric carbon sequestration (i.e., to identify/quantify significant increase in iron-induced carbon export fluxes into intermediate/deeper waters) in the Southern Ocean, (3) determination the environmental conditions that would maximize effectiveness of artificial OIF, and (4) monitoring quantitatively and qualitatively short- and long-term possible side effects derived from previous artificial OIF experiments. With the purpose, we have also added some sentences to discuss why in/near the eastern Bransfield Basin was considered for the site of KIFES based on following three criteria: (1) possibility of diatom bloom, (2) proximity to meso-scale eddies, and (3) availability of historical oceanographic data and to establish the hypothesis that input of bioavailable iron allowing an increase in productivity and export would have led to the massive enhancement of the diatom flux in this basin and an artificial OIF in the diatom-dominated region with high sinking rates near the eastern Bransfield Basin will be more effective for carbon export compared to the previous artificial OIF experiments conducted in the Southern Ocean. Specific plans for KIFES experiment (e.g., duration, patch size, and measurement methods) in Section 5.2 A plan for the future: KIFES (from line 38, page 27 to line 30, page 29) have been modified based on Section 4 Future: Designing future OIF experiment.

**14** *Overall introduction to OIF and statement of the purpose of the present paper.*

☛ We have modified some sentences to define effectiveness of OIF and to introduce purpose of this paper in Section 1 Introduction (from line 1, page 3 to line 15, page 4).

**15** *A brief overview of each of the experiments, maybe written as a historical narrative (1–2 pages) that describes how the various experiments built on each other and what the main hypotheses were that each was designed to address. This section can be used to highlight the different physical and biogeochemical conditions of each experiment, and also highlight the main biogeochemical responses and findings. This experiment-by-experiment approach might help to give the reader are more integrated understanding of each experiment than the current parameter-by-parameter approach used throughout Section 2. The section could then end with a paragraph highlighting the key outstanding questions that future experiments (including KIFES) need to address. These include questions relating to the amount of carbon sequestration, trace gas production, and plankton community shifts.*

☞ Good point. Based on the Reviewer's comment, overall we have reorganized Section 2. Also, please refer Responses **2**–**11**.

**16** *A detailed discussion of each of these questions in turn, highlighting why the previous 13 experiments have failed to reach consensus, and what needs to be done to move our understanding forward. This needs to be an issue-based discussion, for example going into real detail about how carbon fluxes need to be measured, which experiments managed to take these measurements (but failed to find effects), which experiments were maybe hampered by size and/or duration, and also a discussion of the uncertainties relating to each method (e.g. methodological problems with sediment traps, issues with the thorium technique, problems with the estimation of net community production from O2:Ar ratios, etc.).*

☞ Thank you for pointing out this deficiency. We have added the discussion about "why the previous 13 experiments have failed to reach consensus and which experiments were maybe hampered by size and/or duration" to Section 2.5 Summary of the significant results from aOIF experiments (from line 1, page 15 to line 25, page 16) and Section 4 Future: Designing future aOIF experiments (from line 39, page 24 to line 7, page 25). What needs to be done to move our understanding forward was discussed in Section 3 Present: Unanswered aOIF questions - export flux, possible side effects, and international law (from line 27, page 16 to line 24, page 22). Also, please refer Response **9**. We have also created new Section 3.1 Export flux measurement methods (from line 9, page 17 to line 36, page 18) to discuss "how carbon fluxes need to be measured, which experiments managed to take these measurements, and the uncertainties relating to each method". Also, please refer Response **7**.

**17** *A section that reaches specific conclusions and makes recommendations about the design of future experiments.*

☞ Thank you for suggestion. Please refer Response **12**.

**18** *Specific proposal for KIFES and description of the logic for conducting this in the Bransfield Strait. Do the authors have some preliminary altimetry images to show stable eddies in this region?*

☞ Please refer Response **13** for "specific proposal for KIFES and description of the logic for conducting this in the Bransfield Strait".

- For stable eddies in the Bransfield Strait, Thompson et al. (2009) showed that a large standing eddy (~40 km in diameter) was centered at ~62°S and 54°W and remained for ~30 days using historical drifters released during the period 1989–2005, and 40 drifters released in February 2007 as part of the Antarctic Drifter Experiment: Links to Isobaths and Ecosystems project (Fig. R1).

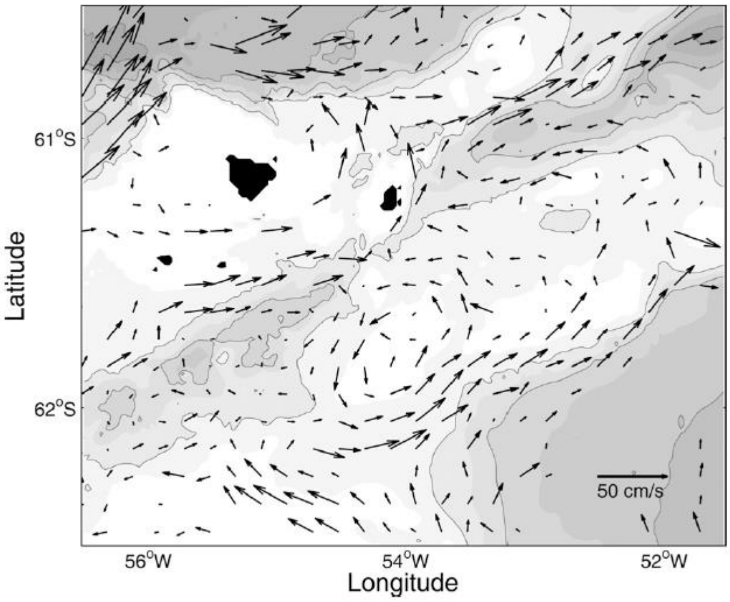


Fig. R1 The mean velocity field for historical drifters released during a period between 1989 and 2007 and forty drifters released in February 2007 as the Antarctic Drifter Experiment: Links to Isobaths and Ecosystems project. The bin size is 0.1° lat x 0.2° lon. The shading indicates bathymetry with color change every 500 m and contour lines at every 1000 m between 1000 m and 4000 m depth (from Thompson et al., 2009).

- Altimetry images obtained from Archiving, Validation and Interpretation of Satellite Oceanographic (AVISO) (https://www.aviso.altimetry.fr/) also show stable eddies (>~50 km in diameter) near/in the eastern Bransfield Strait (Fig. R2). This image is Level-4 sea level anomaly daily image with a spatial resolution of 0.25°. The reference period of the sea level anomaly is based on a 20-year (1993–2012) period.

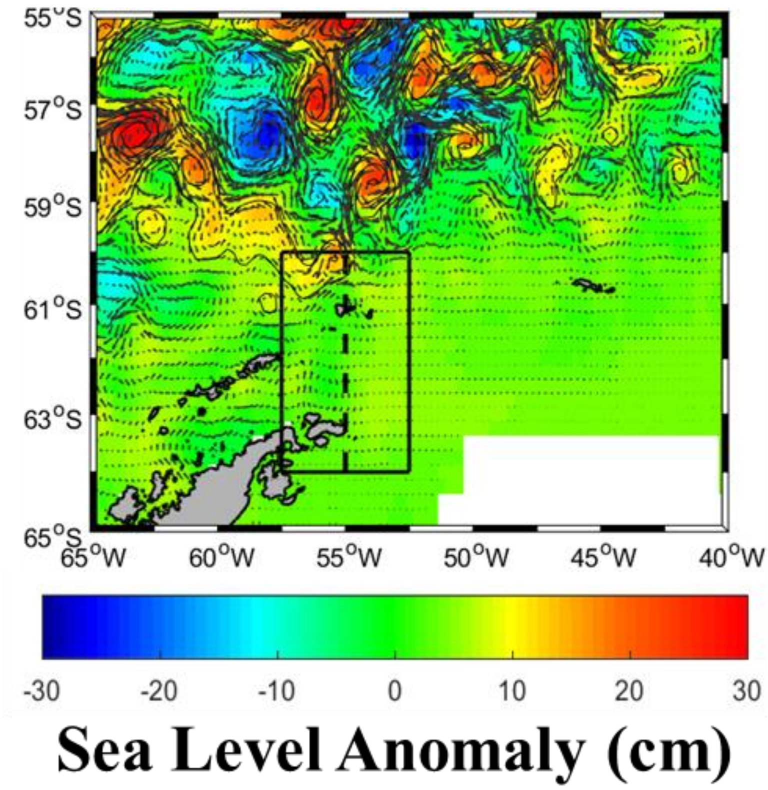


Fig. R2 Sea level anomaly (cm) image in 20-Jan-2015 (https://www.aviso.altimetry.fr/).

**Reviewer #2**

**-General Comments:**

**19** *The question of why the outcomes of previous experiments were so different and how this new project could improve on past experience is only superficially addressed. What are the hypothesis? how the KIFES project improves on previous experiments? and why?*

☛ Good point. We have revised Section 5.1 Background - Bransfield Basin to describe more specifically "what are the hypothesis and how the KIFES project improves on previous experiments" (from line 34, page 26 to line 36, page 27). Also, please refer Response **13**.

**20** *In the same line of thought, the knowledge gained by artificial compared to natural iron experiments (within the context of geoengeneering and potentially negative side-effects) could also be more thoroughly analyzed. As an example, one would be hard pressed to find 'potential long term negative effects' by studying the naturally fertilized systems in the Southern Ocean as these systems are key to sustaining Southern Ocean food webs and biogeochemistry.*

☛ Thank you for suggestion. We have added some sentences about "the knowledge that could be gained by artificial compared to natural iron experiments" in Section 4 as follows:

- Section 4 Future: Designing future aOIF experiments (from line 40, page 22 to line 12, page 23):

"The nOIF experiments have also produced much higher carbon sequestration rates than the small-scale aOIF experiments (Morris and Charette, 2013). Furthermore, the results from nOIF experiments do not support the potential negative impacts proposed for OIF experiments, even at larger scales (Belviso et al., 2008). However, these nOIF results do not guarantee that aOIF as a geoengineering approach is able to achieve the high effectiveness associated with carbon sequestration and enable a simple scaling-up as a prediction tool, because the nOIF experiments differ from the aOIF experiments in the mode of iron supply. In particular, nOIF is a continuous and slow process and its iron source is based on the upwelling of iron-rich subsurface waters to the surface layer, whereas aOIF is intended to be episodic, with massive short-term iron additions (Blain et al., 2007). In addition, in nOIF it is difficult to accurately identify iron sources due to the complexity of the system, whereas in aOIF there is quantitative and qualitative information about iron additions and sources (Blain et al., 2008). Contrary to the results of aOIF experiments in the SO (e.g., SOIREE and SOFeX-N), no increase in DMS emissions was found in nOIF experiments in the SO (i.e., Kerguelen Ocean and Plateau compared Study: KEOPS) (Belviso et al., 2008), suggesting that it might be difficult to identify the potential long-term negative effects of aOIF by studying the naturally fertilized systems in the SO."

**-Specific Comments:**

**21** *In order to simplify comparison, I would recommend to first group the experiments by region with HNLC regions first (Eq. Pac, Subarctic Pac. SO, North Atlantic) and then by date at which they took place in all figures and tables.*

☛ Thank you for your recommendation. We presented the data "by region with HNLC regions (Equatorial Pacific-Southern Ocean-Subarctic North Pacific-North Atlantic) first and then by date at which they took place" in Tables 1–5 (pages 44–52), Figure 4 (page 58) and Figures 6–7 (pages 60–61).

**22** *Table 2: The authors definition of 'limitations' is somewhat unusual. Finding no export is not a 'limitation', just a result that might not support the iron hypothesis. Limitation would be for instance that the experiment did not last long enough to see the terminal phase of the bloom when most export would occur.*

☛ We have removed the results that might not support the iron hypothesis in "limitations" from Table 2 (page 47–48). We have added limitations for experiment design in "limitations".

**23** *Page 13, lines 17-22: Why do the authors focus only on N2O and DMS. From the previous paragraphs, there are many more 'issues' to focus on (those include export, plankton assemblage composition (toxic species), production of other greenhouse gazes, reaction of upper trophic levels. All those are poorly understood.*

☛ Thank you for pointing out this deficiency. Please refer Response **10**.

**24** *Page 16, lines 19-26: The authors would strengthen their case by present scientific evidence to the claim that March is the ideal period (i.e the late growth season can also be challenging due to increased zooplankton biomass and potential Si limitation). Also the 'best' period is most probably linked to the location.*

☛ We agree. PP in the SO, a representative HNLC region, is subject to co-limitation by micro/macro-nutrients (i.e., iron and/or silicate) and light availability (Mitchell et al., 1991). In the south PF of SO, phytoplankton blooms usually occur during the early summer (i.e., from late December to early January) due to the increasing nutrient flux from the subsurface waters to the surface waters by the shoaling of MLD, along with the receipt of sufficient solar radiation (Moore and Abbott, 2002). Prior to December, phytoplankton growth is mainly limited due to light availability (Mitchell et al., 1991; Veth et al., 1997; Abbott et al., 2000), while after January (i.e., during late summer and early autumn from February to March) it is mainly limited due to silicate availability. In previous aOIF experiments in the SO that have been conducted between spring and early autumn, PP was mainly limited by iron and/or silicate availability rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011). In addition, the grazing pressure of mesozooplankton (i.e., copepods) on large diatoms was also a major limiting factor in diatom production (Coale et al., 2004; Martin et al., 2013), and was generally higher during late summer and early autumn (February to March) (Le Quéré et al., 2016). Therefore, by considering the key factors (i.e., micro/macro nutrient availability, light availability, and grazing pressure) controlling PP in the SO, we have modified the most appropriate timing for an aOIF experiment to start in the SO from 'March' to 'late

December–early January' in "When" paragraph in 4 Future: Designing future aOIF experiments (from line 37, page 23 to line 11, page 24).

**25** *Page 17, lines 1-3: Similarly, the planning of the length of the experiment could also be dealt with in a more robust manner and take into account the longevity of the fertilization signal from previous studies (after the patch was left) and include the fact that new autonomous observation technology is available.*

☛ Thank you for comments. We have modified "How long" paragraph in 4 Future: Designing future aOIF experiments (lines 12–32, page 24). SOFeX-S experiments didn't show large increase in export fluxes compared to natural fluxes due to insufficient experiment period (28 days) to cover the termination of phytoplankton bloom. However, only EIFEX (experiment period: 39 days), which did fully monitor all the phases of phytoplankton bloom from onset to termination, showed high export fluxes compared to outside-patch fluxes and this increase in export fluxes occurred between day 28 and day 32 after iron addition. Further, SOIREE showed the longest iron-induced bloom (i.e., the longevity of >40 days). Therefore, experiment period should be at least >~40 days based on the previous OIF experiments.

**26** *Page 17, lines 13-21: I am not sure I understand the point of this paragraph.*

☛ We have removed this paragraph and rewrote Section 5 (from line 33, page 26 to line 7, page 30). Also, please refer Response **13**.

**27** *Table 1: - The description in the legend does not seem to mirror the table headings: Background Fe =Initial Fe in the heading; Fe concentrations after Fe addition = After Fe; ...etc...- 'Day of Fe addition from the beginning of OIF experiment' refers to what? Duration of Fe addition? Or time between start of the experiment and 1st Fe addition?- 'Period' should be 'Duration' instead.- In the title HNLCLSi could be explained as it is not a commonly used acronym.*

☛ We apologize for this confusion. We have revised the legend of Table 1 (lines 1–3, page 44). We have also added annotation to explain "HNLCLSi" (line 1, page 46).

**28** *Table 2: In the title 'limitation' should be 'limitations' (plural). Objectives and name of the experiments are not aligned. This can lead to confusion.*

☛ We revised them in Table 2 (pages 47–48).

**29** *Table 3 legend: 'Changes of chemical parameters…' should be 'Initial conditions and changes (Δ values) in* *chemical parameters during the OIF experiments'.*

☞ We revised it (lines 1–2, page 49).

**30** *Table 4 legend: replace with 'Response of biological parameters to iron fertilization (maximum difference between initial conditions and conditions after fertilization). Note that PP (mg C $m^{-2}$ $d^{-1}$) was estimated by multiplying PP (mg C $m^{-3}$ $d^{-1}$ ) with mixed layer depth (m)'.*

☞ We apologize for the confusion. Maximum in Table 4 legend indicates maximum values after fertilization. To prevent any confusion, we have replaced 'Maximum' with 'After' in Table 4 heading and 'Changes of biological parameters from initial to after (maximum) concentrations by OIF experiments. Note that *PP (mg C $m^{-2}$ $d^{-1}$) was estimated by multiplying PP (mg C $m^{-3}$ $d^{-1}$) with mixed layer depth (m).' with 'Initial values of biological parameters and the values after fertilization. Note that maximum values were attained after fertilization.' in Table 4 legend (line 1, page 50).

**31** *Table 5: Data and methods are not aligned in the table. This can lead to confusion as to which method was used to estimate fluxes during the experiments.*

☞ Thank you for comments. We removed method description column from Table 5 (page 52). However, we left method column because export fluxes estimates depend on measurement methods. Please refer Response **16** for discussion about export flux measurement methods

**32** *Table 5 legend: replace with Ïnitial and maximum export fluxes (mg C m-2 d-1) and corresponding depth in and outside the fertilized patch of OIF experiments. Values in brackets correspond the day of measurement after fertilization."*

☞ We revised it (lines 1–3, page 52).

**33** *Table 5: Export values for the SERIES out patch seem wrong, shouldn't it be 120/48 same values as the initial in-patch values?*

☞ Boyd et al. (2004) showed that 50 m 'outside-patch' export fluxes were 192 mg C $m^{-2}$ $d^{-1}$ on day 3 and 139 mg C $m^{-2}$ $d^{-1}$ on day 15 with deployment of drifting trap. We defined initial export fluxes in SERIES experiment as export fluxes on day 3 during SERIES experiment. In-patch export flux on day 3 was measured in patch center while outside-patch export flux on day 3 was measured in the surrounding waters. Therefore, in-patch export flux on day 3 (~120 mg C $m^{-2}$ $d^{-1}$) was different from outside-patch export flux on day 3 (192 mg C $m^{-2}$ $d^{-1}$).

**34** *Figure 5: the photograph in panel e should be in panel c and vice versa.*

☛ We changed the photograph in panel e to panel c in Figure 5 (lines 20–26, page 53).

**35** *Figures 6 & 7: For comparison purposes it would be helpful to present the data on OIFs grouped by regions rather than the time-sequence in which the experiments took place. As well as maybe demarcate (maybe using vertical lines) each regions (i.e. Eq Pac/Sub. Pac/SO) in the graphs.*

☛ Please refer Response **21**.

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**Abstract.** Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric $CO_2$ concentrations, which have, in turn, had an impact on climate leading to global warming and ocean acidification. Various approaches have been proposed to reduce atmospheric $CO_2$ concentrations. The 'Martin (or Iron) Hypothesis' suggests that ocean iron fertilization (OIF) could be an effective method for stimulating oceanic carbon sequestration through the biological pump in iron-limited, high-nutrient, low-chlorophyll regions. To test the Martin hypothesis, 13 artificial OIF (aOIF) experiments have been performed since 1990 in the Southern Ocean (seven experiments), in the subarctic Pacific (three experiments), in the equatorial Pacific (two experiments), and in the subtropical Atlantic (one experiment). These aOIF field experiments have demonstrated that primary production can be significantly enhanced by the artificial addition of iron. However, the effectiveness of export production (i.e., the export of carbon from surface waters into intermediate/deep waters) revealed by the aOIF experiments was unexpectedly low compared to that achieved by natural phytoplankton blooms, except in the Southern Ocean European Iron Fertilization Experiment. These results, including possible side effects (e.g., changes in climate-relevant gas emissions and an increase in toxic phytoplankton species) have been debated amongst those who support and oppose aOIF experimentation, but many questions remain. In the context of increasing global and political concerns associated with climate change, it is valuable to examine the validity and usefulness of the aOIF experiments. To maximize the effectiveness of aOIF experiments under international OIF regulations in the future, we suggest a design that incorporates several conditions. (1) Experiments are conducted in the center of an eddy structure when grazing pressure is low and silicate levels are high (e.g., in the case of the Southern Ocean, at the south of polar front during the early summer). (2) Shipboard observations are made during a minimum of ~40 days, with multiple iron injections (iron infusions of ~2,000 kg at least three times, with an interval of ~10–15 days, to fertilize a patch of 300 $km^2$ to obtain a ~2 nM concentration). (3) The iron fertilized patch is traced using both physical (e.g., a drifting buoy) and biogeochemical (e.g., sulfur hexafluoride and the Fv/Fm ratio, where Fm is the maximum chlorophyll fluorescence yield and Fv is the difference between Fm and the minimum chlorophyll fluorescence yield) tracers. (4) A neutrally buoyant sediment trap system and water-column derived $^{234}$Thorium method are employed at two depths (one within the mixed layer and another below it), with autonomous profilers equipped with underwater video profiler and transmissometer to estimate accurately the carbon export flux. (5) The side effects on marine/ocean ecosystems are monitored, including the production of climate-relevant gases (e.g., $N_2O$, dimethyl sulfide, and halogenated volatile organic compounds) and an increase in the abundance of toxic phytoplankton species (e.g., production of domoic acid). Finally, we introduce the scientific aOIF experimental design guidelines for a future Korean Iron Fertilization Experiment in the Southern Ocean.

**Keywords:** Ocean Iron Fertilization; High-Nutrient and Low-Chlorophyll regions; Biological Pump; Phytoplankton; Iron

## 1 Introduction

Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric carbon dioxide ($CO_2$) from ~280 ppm (pre-industrial revolution) to ~400 ppm (present day) (http://www.esrl.noaa.gov/), which has, in turn, led to global warming and ocean acidification (IPCC, 2013) (Fig. 1). As the Anthropocene climate system has rapidly become more unpredictable, the scientific consensus is that the negative outcomes are a globally urgent issue that should be resolved in a timely manner for the sake of all life on Earth (IPCC, 1990, 1992, 1995, 2001, 2007, 2013). The various ideas/approaches that have been proposed to relieve/resolve the problem of global warming (Matthews, 1996; Lenton and Vaughan, 2009; Vaughan and Lenton, 2011; IPCC, 2014; Leung et al., 2014; Ming et al., 2014) largely fall into two categories: (1) reduction of atmospheric $CO_2$ by the enhancement of biological $CO_2$ uptake (including ocean fertilization) and/or the direct capture or storage of atmospheric $CO_2$ through chemically engineered processes, and (2) control of solar radiation by artificial aerosol injection into the atmosphere to augment cloud formation and cloud brightening to elevate albedo (Fig. 2). One of the most attractive methods among the proposed approaches is *ocean fertilization*, which targets the drawdown of atmospheric $CO_2$ by nutrient addition (e.g., iron, nitrogen, or phosphorus compounds) to stimulate phytoplankton growth and, subsequently, carbon export to the deep ocean or sediments via the ocean biological pump (ACE CRC, 2015).

The ocean biological pump is frequently depicted as a single combined process, whereby organic matter produced by phytoplankton during photosynthesis in surface waters is quickly transported to intermediate and/or deep waters (Fig. 3a) (Volk and Hoffert, 1985; De La Rocha, 2007). Although the effectiveness of the biological pump is primarily controlled by the supply of macro-nutrients (i.e., nitrate, phosphate, and silicate) from the deep ocean into the mixed layer leading to new production (Sarmiento and Gruber, 2006), iron acts as an essential micro-nutrient to stimulate the uptake of macro-nutrients for phytoplankton growth (Fig. 3b) (Martin and Fitzwater, 1988; Martin, 1990; Morel and Price, 2003). In the subarctic North Pacific (NP), equatorial Pacific (EP), and Southern Ocean (SO), which are well known as high-nutrient and low-chlorophyll (HNLC) regions (Figs. 4a and b), phytoplankton cannot completely utilize the available macro-nutrients (particularly nitrate) for photosynthesis due to a lack of iron. As a consequence, primary production (PP) in these HNLC regions is relatively low, despite the high availability of macronutrients (in particular nitrate and phosphate) (Figs. 4a and b).

Analyses of trapped air bubbles in Arctic/Antarctic ice cores have revealed that atmospheric $CO_2$ (~180 ppm) during the Last Glacial Maximum (LGM; ~20,000 years ago) was much lower than during pre-industrial times (~280 ppm) (Neftel et al., 1982; Barnola et al., 1987; Petit et al., 1999). Over the last 25 years, several hypotheses have been proposed to explain the lowered atmospheric $CO_2$ level during the LGM (Broecker, 1982; McElroy, 1983; Falkowski, 1997; Broecker and Henderson, 1998; Sigman and Boyle, 2000). Dust inputs are generally regarded as a major natural iron source for ocean fertilization, and Martin (1990) hypothesized that during the LGM increased dust inputs relieved iron-limitation and, thereby, substantially enhanced the biological pump in HNLC regions, particularly in the SO (Fig. 3b). Since Martin's hypothesis was first published, there has been an enormous interest in ocean iron fertilization (OIF) because only a small amount of iron (C:Fe ratios = 100,000:1, Anderson and Morel, 1982) is needed to stimulate a strong phytoplankton response. Therefore, much of the investigative focus has centered on the artificial addition of iron to HNLC regions as a means of enhancing carbon fixation and subsequent export via the biological pump (ACE CRC, 2008).

To test Martin's hypothesis, two natural OIF (nOIF) and 13 artificial OIF (aOIF) experiments have been performed to date in the subtropical North Atlantic (NA), EP, subarctic NP, and SO (Blain et al., 2007; Boyd et al., 2007; Pollard et al., 2009; Strong et al., 2009) (Fig. 4a and Table 1). These OIF experiments demonstrated, particularly for the SO, that PP could be significantly increased after iron addition (de Baar et al., 2005; Boyd et al., 2007). However, for aOIF to be considered as a useful geoengineering approach (IPCC, 2007), in the long run, the most critical issue is whether the substantial amounts of organic carbon produced by aOIF in the surface waters lead to a significant export to intermediate/deep layers and long-term

(~1,000 years) storage (Fig. 3c) (Lampitt et al., 2008). A high carbon export was observed in the nOIF experiments in the SO near the Kerguelen Plateau and Crozet Islands (Blain et al., 2007; Pollard et al., 2009). However, all aOIF experiments have shown unexpectedly low carbon exports compared to natural systems (de Baar et al., 2005; Boyd et al., 2007), except for the SO European Iron Fertilization Experiment, EIFEX (Smetacek et al., 2012). The results of these experiments, as well as the potential side effects (e.g., $N_2O$ production and development of hypoxia) (Fuhrman and Capone, 1991), have been scientifically debated amongst those who support and oppose OIF experimentation (Chisholm et al., 2001; Johnson and Karl, 2002; Lawrence, 2002; Buesseler and Boyd, 2003; Smetacek and Naqvi, 2008; Williamson et al., 2012).

In the context of increasing global (social-political-economic) concerns associated with rapid climate change, it is necessary to examine the validity and usefulness of aOIF experimentation as a climate change mitigation strategy. Therefore, the purpose of this paper is to: (1) provide a thorough overview of the aOIF experiments conducted over the last 25 years; (2) discuss aOIF-related important unanswered questions, including carbon export measurement methods, potential side effects, and international law; (3) suggest considerations for the design of future aOIF experiments to maximize the effectiveness of the technique and begin to answer open questions; and (4) introduce design guidelines for a future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project.

## 2 Past: Overview of previous aOIF experiments

A total of 13 aOIF experiments have been conducted in the following areas: 12 experiments were conducted in the three main HNLC (i.e., nitrate >~10 μM) regions: two in the EP, three in the subarctic NP, and seven in the SO (Table 1, Figs. 4a and b). One experiment was conducted in the subtropical NA, known to be a low-nutrient and low-chlorophyll (LNLC) (i.e., nitrate <1 μM) region. These aOIF experiments have been conducted with various/multiple objectives/hypotheses to investigate the biogeochemical responses of ocean environments to artificial iron additions (Table 2). This overview of past aOIF experimentation begins in Section 2.1, with a presentation of the reasons why each experiment was performed and the main hypotheses (Table 2). The unique ocean conditions for the various experiments are described in Section 2.2. Iron addition and the tracing of iron are described in Section 2.3. The biogeochemical responses to the aOIF experiments are presented in Section 2.4, and finally the significant findings from these experiments are summarized in Section 2.5.

### 2.1 Objectives/hypotheses of previous aOIF experiments

#### 2.1.1 Equatorial Pacific

Initially, Martin's hypothesis was supported by the results of laboratory and shipboard iron-enrichment bottle experiments (Hudson and Morel, 1990; Brand, 1991; Sunda et al., 1991; DiTullio et al., 1993; Hutchins et al., 1993). However, the extrapolation of these results based on the lower trophic levels in a marine ecosystem to higher community levels has been strongly criticized due to possible underestimates in grazing forcing and containment effects. To deal with these issues, *in situ* iron fertilization experiments at the whole-ecosystem level are required. Under the hypothesis that artificial iron addition would increase phytoplankton productivity by relieving iron limitations on phytoplankton in HNLC regions, the first aOIF, Iron Enrichment Experiment (IronEx-1), was conducted over 10 days in October 1993 in the EP where high intensity light and warm temperatures would assist rapid phytoplankton growth (Table 1 and Fig. 4a) (Martin et al., 1994; Coale et al., 1998).

However, the magnitude of the biogeochemical responses in IronEx-1 was not as large as expected (Martin et al., 1994). Three hypotheses were advanced to explain the weak responses observed: (1) the possibility of other unforeseen micro-nutrient (e.g., zinc, cadmium, and manganese) or macro-nutrient (e.g., silicate) limitations, (2) the short residence time of bioavailable iron in the surface patch due to an unstable water-column structure, and (3) the extremely high grazing pressure (Cullen, 1995). To test the three hypotheses, a second aOIF experiment, IronEx-2, was conducted in May 1995 (Coale et al., 1996). The IronEx-2 research cruise investigated the same area for a longer period (17 days), providing more time to collect information about the biogeochemical, physiological, and ecological responses to the OIF experiment.

**2.1.2 Southern Ocean**

The SO plays an important role in intermediate and deep-water formation, and has the potential for carbon sequestration associated with artificial iron addition (Martin, 1990; Sarmiento and Orr, 1991; Cooper et al., 1996; Marshall and Speer, 2012). It is known as the largest HNLC region in the World Ocean and models simulating aOIF have predicted that among all HNLC regions, the effect of OIF on carbon sequestration is greatest in the SO (Sarmiento and Orr, 1991). However, a simple extrapolation of the IronEx-2 results to the SO was not deemed appropriate because of the vastly different environmental conditions (Coale et al., 1996) and, therefore, this basin became the next region selected for an aOIF experiment (Frost, 1996). With the hypothesis that iron and light availability may act as key factors that control phytoplankton dynamics, community structure, and grazing in the SO, the Southern Ocean Iron Release Experiment (SOIREE) (Table 1 and Fig. 4a), which was the first *in situ* aOIF experiment performed in the SO, took place in February 1999 (13 days) in the Australasian-Pacific sector (Boyd et al., 2000).

The following year, a second aOIF experiment in the SO, EisenEx ('Eisen' means iron in German), was performed in November within an Antarctic Circumpolar Current eddy in the Atlantic sector (Smetacek, 2001). This region is considered to have a relatively high iron supply, which is supported by dust inputs and sea-ice melt (de Baar et al., 1995; Quéguiner et al., 1997; Smetacek et al., 2002). EisenEx was designed to test the hypothesis that atmospheric dust, an important source of iron in ocean environments, might have led to a dramatic increase in ocean productivity during the LGM due to the relief of iron-limiting conditions for phytoplankton growth.

In addition to iron availability, the supply of silicate is also considered to be an important factor controlling PP in the SO. Silicate-requiring diatoms, which are large-sized phytoplankton, have an important role in the biological pump and are responsible for ~75% of the annual PP in the SO (Tréguer et al., 1995). The silicate concentrations in the SO have a decreasing northward gradient, in particular, on either side of the Antarctic Polar Front (PF), with low silicate concentrations (<5 μM) in the sub-Antarctic waters north of the PF (<61°S) and high silicate concentrations (>60 μM) to the south of the PF (Fig. 4c). Therefore, to address the potential for iron and silicate interactions to regulate the diatom bloom, two aOIF experiments were conducted during January–February 2002 in two distinct regions: the Southern Ocean iron experiment-north (SOFeX-N) and -south (SOFeX-S) of the PF (Table 1) (Coale et al., 2004; Hiscock and Millero, 2005). In these two experiments, it was hypothesized that conditions that provided sufficient silicate and iron would lead to high diatom production, while sufficient iron alone would not lead to a diatom bloom (Coale et al., 2004).

Two years later, the Surface Ocean Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange (SAGE) experiment was conducted during March–April 2004 (15 days) in sub-Antarctic waters, which are HNLC and low silicate concentration waters (HNLCLSi). The aim was to determine the response of phytoplankton dynamics to iron addition in an HNLCSi region (Fig. 4c) (Law et al., 2011). SAGE was designed with the assumption that the response of phytoplankton blooms to artificial iron addition could be detected by enhanced air-sea exchanges of climate-relevant gases (e.g., $CO_2$ and dimethyl sulfide (DMS)) (Harvey et al., 2010; Law et al., 2011).

These early aOIF experiments demonstrated clear increases in phytoplankton biomass, but the association with export production (i.e., exported carbon from the surface waters into intermediate/deep waters) was obscure (de Baar et al., 2005;

Boyd et al., 2007). Therefore, to determine if aOIF could increase export production, EIFEX was conducted during February–March 2004 in a cyclonic eddy core near the PF (Fig. 5). Because it was designed to investigate export production, EIFEX was a much longer experiment (39 days) compared to earlier studies (~28 days or less) (Smetacek et al., 2012).

To trace the fate of an iron-stimulated phytoplankton bloom and deep carbon export, the Indo-German iron fertilization experiment (LOHAFEX; 'Loha' is iron in Hindi) was conducted during January–March 2009 (40 days), also in a PF cyclonic eddy (Smetacek and Naqvi, 2010; Martin et al., 2013).

#### 2.1.3 Subarctic North Pacific

By the 20th century, the subarctic NP was the only HNLC region in which an aOIF experiment had not been performed (Table 1) (de Baar et al., 2005; Boyd et al., 2007). The subarctic NP shows a strong longitudinal gradient in aeolian dust deposition (i.e., high dust deposition in the west, but low in the east) (Duce and Tindale, 1991; Tsuda et al., 2003; Takeda and Tsuda, 2005), which is different from the other two HNLC regions (i.e., EP and SO). To investigate the relationship between the phytoplankton biomass/community and dust deposition, the Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1 (SEEDS-1) was conducted in July–August 2001 (13 days) in the western subarctic gyre (Tsuda et al., 2003, 2005). In 2004, the experiment was repeated (SEEDS-2) in almost the same location and season. In the intervening year, 2002, the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) was performed in July–August (25 days) in the Gulf of Alaska (representing the eastern subarctic gyre ecosystem) to compare the response of phytoplankton in this area with that in the western subarctic (Boyd et al., 2004, 2005). The SEEDS experiments focused on changes in phytoplankton composition, vertical carbon flux, and climate-relevant gas production stimulated by artificial iron addition (Tsuda et al., 2005, 2007). The main objective of SEEDS-2 and SERIES was to determine the most significant factor (i.e., nutrient supply and/or grazing forcing) controlling the iron induced phytoplankton bloom from its beginning to its end (Tsuda et al., 2003; Boyd et al., 2004).

#### 2.1.4 Subtropical North Atlantic

Unlike HNLC regions, PP in LNLC regions, which are predominantly occupied by $N_2$ fixers, is generally co-limited by phosphate and iron (Mills et al., 2004). To investigate the impact of iron and phosphate co-limitation on PP, the *in situ* phosphate and iron addition experiment (FeeP) was conducted by adding both phosphate and iron in a LNLC region of the subtropical NA during April–May 2004 (21 days) (Rees et al., 2007).

### 2.2 Environmental conditions prior to iron addition

The initial environment (~1–7 days before iron addition) can affect the outcome of an aOIF experiment, and the experiments described above were conducted under a wide range of physical and biogeochemical conditions. We considered the similarities and differences in these environments according to the physical and biogeochemical properties of the sites (Steinberg et al., 1998; Coale et al., 1998; Bakker et al., 2001; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Cisewski et al., 2008; Harvey et al., 2010; Cavagna et al., 2011) (Fig. 6, Tables 3 and 4).

#### 2.2.1 Equatorial Pacific

The first two aOIF experiments, IronEx-1 and IronEx-2, which were both conducted in the EP, were performed in different seasons (i.e., IronEx-1: October, IronEx-2: May). However, the initial surface physical conditions were rather similar, with warm temperatures (mean ± SD = 24.1 ± 1.2°C; SD represents standard deviation), high surface photosynthetic available radiation values (~51.7 ± 2.1 mol $m^{-2}$ $d^{-1}$), and shallow mixed layer depths (MLDs) (27.5 ± 2.5 m) (Figs. 6c and d) (Coale et al., 1996; Coale et al., 1998; Steinberg et al., 1998; de Baar et al., 2005).

The initial surface biogeochemical conditions were high nutrients (i.e., nitrate = 10.6 ± 0.2 µM, phosphate = 0.9 ± 0.06 µM, and silicate = 4.5 ± 0.6 µM) and low chlorophyll-a concentrations (0.2 ± 0.05 mg $m^{-3}$) (Tables 3 and 4). The pico-phytoplankton (0.2–2.0 µm) community, including *Synechococcus* and *Prochlorococcus*, was dominant (Martin et al., 1994; Coale et al., 1996; Cavender-Bares et al., 1999). Initial surface nutrient concentrations were relatively low compared with other ocean basin aOIF sites (Table 3 and Fig. 6e). Initial photosynthetic quantum efficiency (i.e., Fv/Fm ratio, where Fm is the maximum chlorophyll fluorescence yield and Fv is the difference between Fm and the minimum chlorophyll fluorescence yield), which is widely used to determine the degree to which iron is the limiting nutrient for phytoplankton growth (the Fv/Fm ratio ranges from 0.2 to 0.65 where conditions are less iron limited as Fv/Fm approaches 0.65), was less than ~0.3 (Fig. 6g and Table 4), suggesting severe iron limitation (Behrenfeld et al., 1996; Barber and Hiscock, 2006; Aiken et al., 2008). In aOIF experiments, the initial surface partial pressure of $CO_2$ ($pCO_2$) has been recorded using continuous shipboard measurement systems (Wanninkhof and Thoning, 1993; Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Takeda and Tsuda, 2005; Smetacek et al., 2005; Wong et al., 2006; Tsumune et al., 2009; Currie et al., 2011). In the EP, initial $pCO_2$ values were 504.5 ± 33.5 µatm, which were much higher than those observed in the SO (355.6 ± 11.7 µatm) or the subarctic NP (370.0 ± 16.3 µatm) (Table 3) (Steinberg et al., 1998).

### 2.2.2 Southern Ocean

The initial physical conditions for the aOIF experiments in the SO (SOIREE, EisenEx, SOFeX-N/S, EIFEX, SAGE, and LOHAFEX) were very different from those found in the EP; MLDs were much deeper (57.9 ± 19.2 m) (Fig. 6c) and sea surface temperature (SST) was much lower (4.7 ± 3.4 °C) (Fig. 6d). During SOFeX-N/S, which were conducted along the same line of longitude, on either side of the PF, there were distinct differences in SST: 5.0°C in SOFeX-N and –0.5°C in SOFeX-S (Coale et al., 2004). SAGE was the northernmost of the aOIF experiments in the SO (Table 1) and, therefore, had the highest SST (11.5°C) (Harvey et al., 2010).

The regions used for the aOIF experiments were selected following preliminary surveys to confirm that the sites were subject to HNLC conditions, i.e., nitrate concentration (>~10 µM) and chlorophyll-a concentration (<1 mg $m^{-3}$). Initial nitrate concentrations ranged from 7.9 µM (SAGE) to 26.3 µM (SOFeX-S) (Fig. 6e and Table 3). Among the various aOIF HNLC experiment sites, the SO had the highest initial nitrate concentrations (21.2 ± 5.8 µM), while the EP had the lowest (10.6 ± 0.2 µM). Initial nitrate and phosphate concentrations at aOIF sites in the SO followed a latitudinal gradient, with higher values to the south of 50°S (nitrate: 24.6 ± 1.6 µM and phosphate: 1.6 ± 0.2 µM) and lower values to the north (nitrate: 16.6 ± 6.2 µM and phosphate: 1.1 ± 0.4 µM) (Table 3, Figs. 4b and 6e). The SO presented the full range of initial silicate concentrations for all aOIF experiments, with values ranging widely from ~1.0 µM (SAGE) in the most northernmost site to ~60 µM (SOFeX-S) in the most southernmost (Table 3, Figs. 4c and 6f). With the specific intent of investigating the co-limitation of iron and silicate to diatom blooms, SOFeX-N, SAGE, and LOHAFEX were all conducted in HNLCLSi regions, with initial silicate concentrations less than 2.5 µM (Figs. 4c and 6f) (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013; Ebersbach et al 2014). Initial $pCO_2$ was lowest in the SO (355.6 ± 11.7 µatm) ranging from 330 µatm (SAGE) to 367 µatm (SOFeX-N) (Table 3).

As in the EP, initial SO Fv/Fm values were below ~0.33 (Table 4 and Fig. 6g), indicating a severe iron limitation. Prior to iron addition, initial chlorophyll-a concentrations ranged from ~0.15 to 0.70 mg $m^{-3}$. The maximum SO chlorophyll concentrations were found at EIFEX, which was dominated by a micro-phytoplankton (20–200 µm) community such as diatoms, while the minimum chlorophyll concentrations were observed at SOFeX-N, which was dominated by a nano-phytoplankton (2.0–20 µm) community, such as prymnesiophytes, pelagophytes, and dinoflagellates.

### 2.2.3 Subarctic North Pacific

The subarctic NP aOIF experiments (i.e., SEEDS-1/-2 and SERIES) were performed in regions with high nitrate (15.6 ± 4.0 μM) and low chlorophyll-a concentrations (0.7 ± 0.2 mg $m^{-3}$) (Tables 3 and 4, Figs. 6e and h). Compared with the other aOIF experiments, these subarctic experiments had much higher initial silicate concentrations (27.3 ± 9.6 μM) (Table 3 and Fig. 6f) and shallower MLDs (Fig. 6c). Although SEEDS-1 and SEEDS-2 were conducted in almost the same location and season in the western basin (Tsuda et al., 2007), the MLD in SEEDS-1 (8.5 m) was shallower than in SEEDS-2 (28 m).

Unlike the latitudinal gradients seen in the aOIF experiments in the SO, there were longitudinal gradients in physical and biogeochemical properties in the subarctic NP experiments (Tables 3–4, Figs. 4b–c, and Figs. 6d–h). Initial SSTs in the SO were lower in the western region (7.5°C in SEEDS-1 and 8.4°C in SEEDS-2) than in the eastern region (12.5°C in SERIES) (Fig. 6d). Initial nutrient concentrations were much higher in the west (nitrate: 18.5 ± 0.1 μM and silicate: 34.0 ± 2.2 μM) compared to the east (nitrate: 10 μM and silicate: 14 μM) (Table 3, Figs. 4b–c and 6e–f). There was also a longitudinal gradient in chlorophyll-a concentrations, with relatively high values in the west (SEEDS-1: 0.8 mg $m^{-3}$ and SEEDS-2: 0.8 mg $m^{-3}$) and low in the east (SERIES: 0.4 mg $m^{-3}$) (Fig. 6h). Before the first SEEDS-1 iron infusion, micro-phytoplanktons, such as the pennate diatom "*Pseudo-nitzschia turgidula*", were dominant, whereas the areas for SERIES and SEEDS-2 were exclusively occupied by pico- and nano-phytoplankton, such as *Synechococcus* and haptophytes (Tsuda et al., 2005; Boyd et al., 2005; Sato et al., 2009). Initial Fv/Fm ratios in the subarctic NP aOIF experiments were <0.3, indicating a severe iron limitation (Fig. 6g).

### 2.2.4 Subtropical North Atlantic

One exception to the focus on HNLC study sites was the FeeP experiment, which was conducted in the subtropical NA, a typically LNLC region (Figs. 4a and b, Tables 3 and 4). To test the effects of the co-limitation of iron and phosphate on PP, FeeP was conducted under much lower initial nutrient (nitrate: <0.01 μM, phosphate: ~0.01 μM, and iron: <0.4 nM) and chlorophyll-a (<0.1 mg $m^{-3}$) conditions than any of the other experimental sites (Rees et al., 2007).

## 2.3 Iron addition and tracing methods

### 2.3.1 Iron addition

Iron(II) and sulfate aerosols are ubiquitous in the atmosphere and, therefore, iron-sulfate ($FeSO_4 \cdot H_2O$), a common form of combined iron that enters the ocean environment via dust deposition, has been frequently regarded as a bioavailable iron source during glacial periods (Zhuang et al., 1992; Zhuang and Duce, 1993; Spolaor et al., 2013). Iron-sulfate is a common inexpensive agricultural fertilizer that is relatively soluble in acidified seawater (Coale et al., 1998). Therefore, all aOIF experiments have been conducted by releasing commercial iron-sulfate dissolved in acidified seawater into the propeller wash of a moving ship (Fig. 5), to ensure mixing with surface waters during iron additions.

In general, background dissolved iron concentrations in HNLC regions are <0.4 nM (Table 1). Iron-enrichment bottle incubation experiments performed in deck incubators using ocean water have indicated the maximum phytoplankton growth rates in response to iron additions of 1–2 nM (Fitzwater et al., 1996). In aOIF experiments performed in the ocean, targeted iron concentrations within the MLD have ranged between ~1 to 4 nM, depending on the site (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Bowie et al., 2001; Tsuda et al., 2003; Coale et al., 2004; Nishioka et al., 2005; Law et al., 2006; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012; Martin et al., 2013). If injected iron is well dispersed throughout the mixed layer within 24 hours by convective mixing (Martin and Chisolm, 1992), the amount of added iron required to raise the background iron concentration to the target level can be calculated using a volume estimate (i.e., iron-fertilized water patch area × MLD) (Watson et al., 1991). To minimize uncertainty between the first iron addition and phytoplankton response, aOIF experiments have involved multiple-small iron injections to the surface waters in the study area at ~0.4 to ~1.5 km intervals over a 1–2-day period (Coale et al., 1998). The patch size fertilized by the first iron addition varied from 25 $km^2$ (e.g., FeeP; Iron(II) addition of 1840 kg) to 300 $km^2$ (e.g., LOHAFEX; Iron(II) addition of 2,000 kg), and by the end of these experiments had spread to a maximum ~2500 $km^2$ (Coale et al., 2004; Boyd et al., 2007; Martin et al., 2013) (Table 1, Figs. 6a and b).

During the experiments, dissolved iron concentrations increased to the target ~1.0–4.0 nM (Table 1), but decreased to background concentrations within days. The fast decrease in dissolved iron concentrations indicates that iron was horizontally dispersed and/or rapidly incorporated into particles. These processes occur more rapidly in warmer waters (ACE CRC, 2015). For example, the first aOIF experiment, IronEx-1, showed that the dissolved iron concentration rapidly decreased from 3.6 to 0.25 nM ~2 days after iron addition in the center of the fertilized patch, suggesting a limit to the level required for phytoplankton growth (Gordon et al., 1998). As a result, except for the single iron addition experiments of IronEx-I, SEEDS-1, and FeeP (Martin et al., 1994; Tsuda et al., 2003; Rees et al., 2007), most aOIF experiments have involved multiple iron additions at the patch center, to continuously drive the stimulation of phytoplankton during the experiments. These experiments included: (2 additions) EIFEX, SERIES, SEEDS-2, LOHAFEX (Boyd et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013); (3 additions) IronEx-2, EisenEx, SOFeX-N (Coale et al., 1996; Gervais et al., 2002; Coale et al., 2004; Nishioka et al., 2005); and (4 additions) SOIREE, SOFeX-S, SAGE (Boyd et al., 2000; Coale et al., 2004; Bakker et al., 2005; Harvey et al., 2010) (Table 1).

**2.3.2 Tracing iron-fertilized patch**

To trace the iron-fertilized patch, aOIF experiments have used a combination of physical and biogeochemical approaches. All the aOIF experiments except EIFEX have used sulfur hexafluoride ($SF_6$) as a chemical tracer (Table 1) (Martin et al., 1994; de Baar et al., 2005). The $SF_6$, which is not naturally found in oceanic waters, is a useful tracer for investigating physical mixing and advection-diffusion processes in the ocean environment due to its nontoxicity, biogeochemically inert characteristics, and low detection limit (Law et al., 1998). The injected $SF_6$ is continuously monitored using gas chromatography with an electron capture detector system (Law et al., 1998; Tsumune et al., 2005). Usually only one $SF_6$ injection is necessary because background levels are generally extremely low in the ocean (<1.2 fM; f: femto-, $10^{-15}$) (Law et al., 1998; Law et al., 2006; Martin et al., 2013); however, in the SAGE experiment, with its higher mixing and lateral dilution, there were three injections (Harvey et al., 2010). Although these earlier experiments demonstrated that the injection of artificial $SF_6$ is a useful technique for following iron-fertilized patches, caution is required because artificially high levels of $SF_6$ injection may negatively impact the interpretation of low-level $SF_6$ signals dissolved in seawater via air-sea exchange. These techniques have been widely used to estimate anthropogenic carbon invasion as well as to understand ocean circulation in various ocean environments, with $SF_6$ being an important time-dependent tracer that has a well-recorded atmospheric history (Fine, 2011). Continuous sampling systems, measuring biogeochemical parameters such as Fv/Fm, $pCO_2$, and chlorophyll fluorescence, have also been used as an alternative means of following iron-fertilized patches (Gervais et al., 2002; Boyd et al., 2005; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012). The Fv/Fm ratio displays a particularly rapid increase (within 24 hours) in response to an initial iron addition (Kolber et al., 1994; Behrenfeld et al., 1996; Smetacek et al., 2012), suggesting that it is an easy and convenient tracer for following a fertilized patch.

In addition, surface-drifting buoys equipped with Array for Real-time Geostrophic Oceanography (ARGO) and Global Positioning System (GPS) sensors have been successfully used to track the movement of fertilized patches along with biogeochemical tracers (Coale et al., 1998; Boyd and Law, 2001; Law et al., 2006; Martin et al., 2013). However, floats tend to deviate from the location of fertilized patches under strong wind forcing (Watson et al., 1991; Law et al., 1998; Stanton et al., 1998). NASA airborne oceanographic lidar and ocean-color satellites have also been employed to assess the large-scale effects of iron addition on surface chlorophyll in fertilized patches, as compared to surrounding regions (Martin et al., 1994; Westberry et al., 2013).

### 2.4 Biogeochemical responses

Biogeochemical responses to artificial iron addition, measuring various biogeochemical parameters (e.g., Fv/Fm ratio, chlorophyll-a, PP, nutrients, $CO_2$ variables, and carbon export fluxes), have been investigated in the HNLC regions (Tables 3–5 and Figs. 7–8). The results are important, as they have been used as a basis to determine whether the aOIF is effective. Here we address the biogeochemical response in each of the ocean basins to the aOIF experiments to date.

#### 2.4.1 Equatorial Pacific

The IronEx-1 and 2 experiments, which were conducted in similar initial conditions (refer to Section 2.2.1), presented quite different biogeochemical responses (Tables 3–4 and Fig. 7). In IronEx-1, there were small increases in the Fv/Fm ratio, chlorophyll-a concentration, and PP, but no significant changes in nutrients and $pCO_2$ concentrations (Martin et al., 1994). On the other hand, IronEx-2 found dramatic changes in biogeochemical responses, providing support for Martin's hypothesis (Coale et al., 1996). The extremely different results from the two experiments are likely to be associated with additional iron injections (IronEx-1: no extra addition; IronEx-2: 2 additional injections) and different experimental durations (IronEx-1: 10 days; IronEx-2: 17 days).

The Fv/Fm ratios provided further detail. In IronEx-1 and IronEx-2, Fv/Fm rapidly increased within ~24 hours of iron addition and reached a maximum of ~0.60 on the second day (Table 4) (Barber and Hiscock, 2006; Aiken et al., 2008). While the elevated IronEx-1 Fv/Fm ratios promptly disappeared, indicating a rapid iron loss (perhaps indicative of insufficient iron supply), increased IronEx-2 Fv/Fm ratios were maintained for eight days through multiple iron additions, suggesting that additional iron enrichments are likely to be a determining factor in successfully artificially increasing PP through OIF (Kolber et al., 1994; Behrendfeld et al., 1996).

During IronEx-1, chlorophyll-a concentrations increased significantly (3-fold) reaching a maximum value of 0.65 mg $m^{-3}$ in the first four days following iron addition (Martin et al., 1994). In IronEx-2, surface chlorophyll-a increased <27-fold with a maximum of 4 mg $m^{-3}$ after day 7 (Table 4 and Fig. 7c) (Coale et al., 1996). To quantify the changes in carbon fixation following iron addition, the depth-integrated PP (from the surface to the critical depth, euphotic depth, or MLD) was estimated in the iron-fertilized patches. The depth-integrated PP values increased significantly compared to the initial values. The IronEx-2 $\Delta PP$ (where $\Delta PP = PP_{post\text{-}fertilization\ (postf)} - PP_{pre\text{-}fertilization\ (pref)}$) was the highest (~1800 mg C $m^{-2}$ $d^{-1}$) of all the aOIF experiments discussed here (Table 4 and Fig. 7e).

The increased PP during IronEx-2 was, in turn, accompanied by drawdowns of $pCO_2$ ($\Delta pCO_2 = [pCO_2]_{postf} - [pCO_2]_{pref}$ = -73 µatm) and dissolved inorganic carbon (DIC) ($\Delta DIC = [DIC]_{postf} - [DIC]_{pref}$ = -27 µM) (Table 3 and Fig. 7f) (Steinberg et al., 1998). As the bloom developed, a significant nitrate uptake (e.g., $\Delta NO_3^- = [NO_3^-]_{postf} - [NO_3^-]_{pref}$ = -4.0 µM) was observed (Table 3 and Fig. 7b) and silicate concentrations also gradually decreased from 5.1 to 1.1 µM (i.e., limiting diatom growth) over eight days (Coale et al., 1996; Boyd, 2002). The depletion of macro-nutrients in fertilized patches provides indirect evidence that phytoplankton growth in surface waters is driven by iron fertilization (Boyd and Law, 2001).

Although no phytoplankton community change was observed in IronEx-1, after iron addition in IronEx-2 there was a shift from a pico-phytoplankton dominated community to a micro-phytoplankton dominated community, resulting in diatom-dominated blooms (Behrenfeld et al., 1996; Coale et al., 1996; Cavender-Bares et al., 1999). Diatom biomass increased <70-fold over eight days early in the experiment, compared to a less than a 2-fold increase for the pico-phytoplankton (Landry et al., 2000). The biomass of meso-zooplankton (200–2,000 μm), such as copepods, also increased simultaneously, substantially increasing the grazing effect (~50%) (Coale et al., 1996). However, the grazing force of the increased biomass was insufficient to suppress the diatom bloom over eight days early in the IronEx-2 experiment (Table 4) (Coale et al., 1996). The iron-induced diatom bloom began to decline after day ~8 of the experiment. The decline was probably associated with the combined effects of both the elevated grazing pressure and the onset of nutrient depletion (i.e., limitation in silicate and/or iron) (Cavender-Bares et al., 1999; Boyd, 2002).

To determine whether the biological pump (i.e., export production) is enhanced after iron addition, the export flux of particulate organic carbon (POC) can be estimated using, individually or in combination, chemical tracers such as the natural radiotracer thorium-234 ($^{234}$Th; half-life = 24.1 days) and the stable carbon isotope of particulate organic matter ($\delta^{13}C_{org}$), sediment traps, transmissometers, and underwater video profilers (UVPs) (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). The $^{234}$Th radionuclide has a strong affinity for particles, and the extent of $^{234}$Th removal in the water column is indicative of the export of POC associated with surface PP out of the mixed layer (Buesseler, 1998). IronEx-2 was the first aOIF experiment in which the POC flux was estimated (Bidigare et al., 1999). The $^{234}$Th deficiency from the surface to 25 m was measured in the iron-fertilized patch to estimate iron-stimulated export production in the surface layer (Table 5). However, no $^{234}$Th measurements were made in the unfertilized patch for comparison, and no measurements in the deep ocean were undertaken to demonstrate deep carbon export (Bidigare et al., 1999).

### 2.4.2 Southern Ocean

As in the EP IronEx-1/-2 experiments, there were initial rapid increases in the Fv/Fm ratio within 24 hours of iron addition, indicating that phytoplankton growth was mainly limited by iron availability. Maximum values of the Fv/Fm ratio ranged from 0.5 (SOFeX-N and LOHAFEX) to 0.65 (SOIREE and SOFeX-S) (Table 4 and Fig. 7a). However, the time taken to reach the maximum Fv/Fm ratio was usually longer than ~10 days, i.e., much slower than in IronEx-1/-2 (~2 days) (Boyd and Abraham, 2001; Gervais et al., 2002; Coale et al., 2004; Smetacek et al., 2005; Peloquin et al., 2011; Martin et al., 2013). The slower response time in the SO compared to the EP might be attributed to the colder temperatures (~5°C vs. ~24°C) and/or the deeper MLDs (~60 m vs. ~30 m) (Figs. 6c and d), which were indicative of active physical mixing (Boyd and Abraham, 2001; Boyd, 2002).

The aOIF experiments in the SO recorded >2-fold increases in chlorophyll-a concentrations compared to initial levels (<0.7 mg m$^{-3}$), and maximum values between 1.25 mg m$^{-3}$ (LOHAFEX) and ~3.8 mg m$^{-3}$ (SOFeX-S) were obtained after artificial iron additions (Table 4 and Fig.7c). Satellite observations were used to investigate the changing spatial and temporal distribution of chlorophyll-a concentrations in response to iron fertilization in the fertilized patches compared to the surrounding waters (Boyd et al., 2000; Coale et al., 2004; Boyd et al., 2005; Westberry et al., 2013). For example, spatial changes in chlorophyll-a resulting from SOFeX-N/S iron addition were detected using Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images. The chlorophyll-a image on day 24 after iron addition in the SOFeX-N showed a phytoplankton bloom distribution resembling a long thread with 10-fold higher concentrations (1.0 mg m$^{-3}$) than the surrounding waters (0.1 mg m$^{-3}$), while a chlorophyll-a image on day 20 of SOFeX-S suggested a somewhat broader bloom pattern (0.5 mg m$^{-3}$), with concentrations elevated ~5-fold over the surrounding levels (~0.1 mg m$^{-3}$) (Fig. 7d) (Westberry et al., 2013).

Following artificial iron enrichment in the SO, ΔPP ranged from 360 (SAGE) to ~1356 mg C $m^{-2}$ $d^{-1}$ (SOFeX-N) (Table 4 and Fig. 7e). In SOIREE, EisenEx, and SOFeX-N/S, the PP increased continuously throughout the duration of the experiments (Boyd et al., 2000; Gall et al., 2001a; Gervais et al., 2002; Coale et al., 2004). However, in EIFEX, SAGE, and LOHAFEX there was a significant increase in PP for ~10 (SAGE) – 20 (EIFEX) days in response to the iron addition, and decreasing trends after day ~12 (SAGE) – 25 (EIFEX) due to various influences, such as high export production (e.g., EIFEX), lateral dilution with surrounding waters (e.g., SAGE), and high grazing pressure and active bacterial respiration (e.g., LOHAFEX) (Boyd, 2002; Gervais et al., 2002; Buesseler et al., 2004; Coale et al., 2004; Peloquin et al., 2011; Smetacek et al., 2012; Martin et al., 2013).

Using both microscopes and high-performance liquid chromatography pigment analysis, changes in phytoplankton community affected by iron addition have also been investigated. SO iron additions have resulted in blooms of relatively large-sized phytoplankton (Boyd et al., 2007). During SOIREE and EisenEx, the dominant phytoplankton community shifted from pico- and nano-phytoplankton (e.g., pico-eukaryotes and prymnesiophytes) to micro-phytoplankton (i.e., diatoms) (Gall et al., 2001a; Gervais et al., 2002). In SOFeX-S and EIFEX, diatoms were already the most abundant group prior to iron addition (Coale et al., 2004; Hoffmann et al., 2006). The contribution of large diatoms became especially clear in EIFEX where ~97% of the phytoplankton bloom was attributed to these species (Smetacek et al., 2012). However, no taxonomic shift toward diatom-dominated phytoplankton communities (<5% of total phytoplankton community) was observed in SAGE and LOHAFEX, which were conducted under silicate-limited conditions (Harvey et al., 2010; Peloquin et al., 2011; Martin et al., 2013; Ebersbach et al., 2014). Although SOFeX-N was conducted under low silicate conditions, the diatom biomass increased remarkably making up ~44% of the total phytoplankton community (Coale et al., 2004). This result was partly influenced by the temporary relief of silicate limitation through lateral mixing of the iron-fertilized waters with surrounding waters, with relatively higher silicate concentrations (Coale et al., 2004).

Iron-mediated increases in PP resulted in a significant uptake in macronutrients and $pCO_2$ throughout the aOIF experiments in the SO (except for SAGE) (Table 3, Figs. 7b and f). The $\Delta NO_3^-$ ranged from -3.5 μM (e.g., SOFeX-S) to -1 μM (e.g., EisenEx) and $\Delta pCO_2$ ranged from -38 μatm (e.g., SOIREE) to -7 μatm (e.g., LOHAFEX). Although SOFeX-S had a somewhat greater $\Delta NO_3^-$ (-3.5 μM) and $\Delta pCO_2$ (-36 μatm) than EIFEX ($\Delta NO_3^-$: -1.6 μM and $\Delta pCO_2$: -30 μatm) both results suggested that diatoms were abundant in the two experiments. However, the smaller ΔSi observed during SOFeX-S (-4 μM, compared to EIFEX -11 μM) was associated with a decrease in silicification (i.e., the adjustment of frustule thickness toward thinner frustules) of the dominant diatom species (i.e., *Fragilariopsis* sp.) (Twining et al., 2004). In EIFEX, the ratio of heavily silicified diatoms (e.g., *Thalassiothrix antarctica*) to total diatom biomass increased from 0.24 (day 0) to 0.46 (day 37) leading to the larger ΔSi (i.e., more demand for silicate) (Hoffmann et al., 2006). Interestingly, the biogeochemical responses in SAGE were totally different from those seen in other experiments, in particular of increases in $\Delta NO_3^-$ (+3.9 μM), $\Delta pCO_2$ (+8 μatm), and ΔDIC (+25 μM) (Table 3, Figs. 7b and f). These contrasting results were thought to be the result of entrainment through vertical and horizontal physical mixing into the iron-fertilized patch of the waters, with higher biogeochemical concentrations (Currie et al., 2011; Law et al., 2011).

SOIREE was the first aOIF experiment in the SO to estimate the downward carbon flux into deep waters (Fig. 3c). They used a comprehensive suite of methods such as the deployment of a drifting trap, $^{234}Th$ and $\delta^{13}C_{org}$ estimates derived from high-volume pump sampling, and a beam transmissometer (Nodder and Waite, 2001). However, no measurable change in carbon export was observed in response to iron-stimulated PP (Table 5 and Fig. 8b) (Charette and Buesseler, 2000; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001). During EisenEx, an increased downward carbon flux estimated from $^{234}Th$ deficiency was observed in the iron-fertilized patch as the experiment progressed. However, there were no clear differences between in- and outside-patch carbon fluxes (Buesseler et al., 2005). During SOFeX-S, significantly enhanced POC fluxes below the mixed layer after iron enrichment were obtained from $^{234}$Th observations (Buesseler et al., 2005). However, the absolute magnitude of these flux increases was similar to that observed in natural blooms. Uniquely, SOFeX-N used only free-profiling robotic Lagrangian carbon explorers equipped with transmissometers to estimate the downward carbon flux without employing chemical tracers, and observed large POC flux events between day ~27 and ~45 after the first iron addition (Bishop et al., 2004; Coale et al., 2004). However, it was unclear whether surface-fixed carbon was well and truly delivered into intermediate/deep depths. For SAGE and LOHAFEX experiments, which were conducted under silicate limited conditions (Table 3, Figs. 4c and 6f), there was no detection of fertilization-induced export by any method (Table 5) (Peloquin et al., 2011; Martin et al., 2013). This result was likely to be associated with the pico-plankton dominated community, which led to rapid recycling in the mixed layer and less downward carbon flux. In contrast to the other aOIF experiments, EIFEX, which was conducted within the core of an eddy, provided clear evidence of carbon export stimulated by artificial iron addition (Jacquet et al., 2008; Smetacek et al., 2012). During EIFEX, the initial export flux, estimated from $^{234}$Th in the upper 100 m of the fertilized patch, was ~340 mg C m$^{-2}$ d$^{-1}$ (Table 5 and Fig. 8a) (Smetacek et al., 2012). This value remained constant for about 24 days after iron addition. Between day 28 and 32 a massive increase in carbon export flux (maximum of ~1692 mg C m$^{-2}$ d$^{-1}$) was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Table 5 and Fig. 8a). The profiling transmissometer with high-resolution coverage confirmed this result, showing an increase in exported POC below 200 m after day 24. At least half the iron-induced biomass sank (via the formation of aggregates of diatom species, in particular '*Chaetoceros dichaeta*') to a depth of 1,000 m, with a tenfold higher sinking rate (500 m d$^{-1}$), compared to the initial conditions (Smetacek et al., 2012). Significant changes in export production were not found in any of the other aOIF experiments and, therefore, the impact of artificial iron addition on this component of the biological pump needs to be resolved in future OIF experiments (Boyd et al., 2004; Smetacek et al., 2012; Martin et al., 2013).

### 2.4.3 Subarctic North Pacific

The observed increase in the Fv/Fm ratio in response to artificial iron addition in the subarctic NP suggests that the relief in iron limitation may have assisted phytoplankton growth (Table 4 and Fig. 7a). SEEDS-1/-2, which were conducted in the western basin, showed continuous increases in the Fv/Fm ratio, with a maximum value of ~0.4 approximately 10 days after the first iron addition (Tsuda et al., 2003; Tsuda et al., 2007). During SERIES, which was conducted in the eastern basin, the Fv/Fm ratio rapidly increased and reached a maximum value of 0.55 within 24 hours of the first iron addition (Boyd et al., 2005). However, the Fv/Fm ratio returned toward the initial value of <0.3 as the dissolved iron concentrations decreased to background levels (<0.2 nM) after about day 10 (Tsuda et al., 2003; Boyd et al., 2005; Tsuda et al., 2007).

Increases in chlorophyll-a concentrations were detected in the subarctic NP aOIF experiments in both basins after about the fifth day (Tsuda et al., 2003; Boyd et al., 2004; Suzuki et al., 2009). These increases were especially apparent in SEEDS-1, where they reached a maximum value of 21.8 mg m$^{-3}$ (27 times the initial value of 0.8 mg m$^{-3}$) (Table 4 and Fig. 7c). This augmentation was the largest among all the aOIF experiments (Tsuda et al., 2003). The dramatic chlorophyll-a increase observed during SEEDS-1 was partly attributed to the particular range of seawater temperature in the region, which was conducive to diatom growth (i.e., 8–13°C) as well as to the shallower MLD (~10 m), which provided a relatively longer surface water residence time for the additional iron (Figs. 6c and d) (Noiri et al., 2005; Takeda and Tsuda, 2005; Tsumune et al., 2005). During SERIES, chlorophyll-a concentrations increased substantially from the initial value of 0.35 to 5 mg m$^{-3}$ over 17 days, and the second highest concentration of all aOIF experiments was recorded (Table 4 and Fig. 7c) (Boyd et al., 2004). However, on the 18th day there was a downturn in chlorophyll-a as silicate concentrations decreased to <2 μM (Boyd et al., 2005). Although SEEDS-2 was conducted under similar initial conditions to SEEDS-1 (refer to Section 2.2.3), there was a minimal increase in chlorophyll-a (i.e., maximum value of less than 3 mg m$^{-3}$) (Fig. 7c). This smaller increase was thought to be the result of extensive copepod grazing (SEEDS-2 had almost five times more copepod biomass than SEEDS-1) (Table 4) (Tsuda et al., 2007). A similar spread was seen in depth-integrated PP, which increased by 7-fold or more after various iron enrichments in the subarctic NP aOIF experiments (e.g., from 300–420 to 1,000–2,000 mg C $m^{-2}$ $d^{-1}$) (Table 4 and Fig. 7e).

Changes in the composition of phytoplankton groups were investigated in the subarctic NP aOIF experiments. In SEEDS-1 there was a shift from oceanic diatoms (e.g., *Pseudonitzschia turgidula*), with growth rates of 0.5–0.9 $d^{-1}$, to faster-growing neritic diatoms (e.g., *Chaetoceros debilis*, 1.8 $d^{-1}$) (Tsuda et al., 2005). The shift in the dominant phytoplankton species during the SEEDS-1 experiment was an important contributor to what became the greatest aOIF-induced increase in phytoplankton biomass yet recorded. During SERIES, the phytoplankton community changed from *Synechococcus* and haptophytes to diatoms, and the highest SERIES chlorophyll-a concentration (day 17) was associated with a peak in diatom abundance (Boyd et al., 2005). However, during SEEDS-2, no significant iron-induced diatom bloom was observed. Instead, pico-phytoplankton (e.g., phytoflagellates) (67% of the total community) dominated throughout the duration of the experiment due to the heavy grazing pressure on diatoms (Table 4) (Tsuda et al., 2007).

In the subarctic NP experiments, significant decreases in macro-nutrient uptake (i.e., $\Delta NO_3^-$ and ΔSi), ΔDIC, and $\Delta pCO_2$ in response to artificial iron addition were observed (Table 3 and Figs. 7b and f). SEEDS-1, which saw the largest increases in chlorophyll-a concentrations, also had the largest $\Delta pCO_2$ (-130 μatm) and ΔDIC (-58 μM) (Table 3 and Fig. 7f). These changes led, in turn, to the largest $\Delta NO_3^-$ (-15.8 μM) (Fig. 7b) and ΔSi (-26.8 μM) (Table 3) (Tsuda et al., 2003). The second largest increase in the chlorophyll-a concentration was observed in SERIES, where drawdowns of $pCO_2$ (-85 μatm), DIC (-37 μM), nitrate (-8.5 μM), and silicate (-13.6 μM) were recorded. During SEEDS-2, the nitrate concentration decreased remarkably from 18.4 μM to 12.7 μM after day 5; however, there was no significant change in silicate concentrations, which would have been expected as a signal of an iron-induced diatom bloom (Tsuda et al., 2007; Suzuki et al., 2009).

Despite the formation of a massive iron-induced phytoplankton bloom during SEEDS-1, there was no large POC export flux during the observation period (Table 5) (Tsuda et al., 2003; Aono et al., 2005; Aramaki et al., 2009). During SERIES and SEEDS-2, which allowed comprehensive time-series measurements of the development and decline of the iron-stimulated bloom, POC fluxes estimated by the drifting traps in the fertilized patch displayed temporal variations (Boyd et al., 2004; Aramaki et al., 2009). However, the results suggested that only a small part of the decrease in the mixed layer POC was subsequently captured by the drifting trap, and POC flux losses were mainly governed by bacterial remineralization and mesozooplankton grazing (Boyd et al., 2004; Tsuda et al., 2007).

#### 2.4.4 Subtropical North Atlantic

Not much is known about the biogeochemical responses to OIF in the subtropical NA. The FeeP experiment reported that pico-plankton abundances increased after iron and phosphate additions (Rees et al., 2007); however, no other details of the biogeochemical response to iron addition in FeeP have been reported.

### 2.5 Summary of the significant results from aOIF experiments

To test the hypothesis that the addition of iron to the surface layer will effectively reduce atmospheric $CO_2$ by increasing PP and enhancing, in turn, the carbon export flux to the deep ocean, aOIF experiments have usually been conducted in HNLC regions: the EP, SO, and subarctic NP. The one exception was the FeeP experiment, which was performed in the subtropical NA. The initial environmental conditions associated with the physical and biogeochemical properties were determined at these OIF sites over 1–7 days before iron addition to allow the responses to the aOIF to be evaluated and quantified. Preliminary surveys confirmed that all sites, except FeeP in the subtropical NA, were subject to iron-limited HNLC conditions, with typical levels of iron <0.4 nM, nitrate >~10 μM, and chlorophyll-a <1 mg $m^{-3}$. The initial Fv/Fm ratios were <~0.3, suggesting that phytoplankton growth was severely iron-limited. In SEEDS-1, SOFeX-S, and EIFEX, prior to the addition of iron, the micro-phytoplankton (e.g., diatom) community accounted for half of the population and this was thought to be beneficial to the enhancement of export production. In the other experiments, pico- and nano-phytoplankton (e.g., *Synechococcus* and haptophytes) initially dominated; they are associated with rapid recycling in the mixed layer through the microbial loop rather than export production (Michaels and Silver, 1988; Coale et al., 1998; Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; Tsuda et al., 2005; Hoffmann et al., 2006; Tsuda et al., 2007; Harvey et al., 2010; Martin et al., 2013).

Iron-sulfates dissolved in acidified seawater have been commonly used for artificial iron addition because they are both highly bioavailable and inexpensive. The mixture is generally released into the ship's wake over a period of 24 hours. The amount of added iron was determined so to reach a target dissolved-iron concentration (at least >1 nM) by volume (defined as the MLD × patch area). To achieve this, a wide range of 225–2,000 kg was applied. Except in IronEx-1 and SEEDS-1, the experiments used multiple (2–4) iron additions to reinforce the increased iron levels. To trace the iron-fertilized patches, physical tracers (i.e., ARGO or other GPS-tracked drifting buoys) and/or chemical tracers such as $SF_6$ were used. In addition, biogeochemical parameters, such as the Fv/Fm ratio, macro-nutrients, and $CO_2$ variables, were used to detect responses through a comparison of before and after conditions (i.e., $\Delta = [\text{parameter}]_{postf} - [\text{parameter}]_{pref}$). In particular, it should be noted that the Fv/Fm ratios promptly increased from <~0.3 to 0.56 (± 0.08) in the two days following iron addition, indicating a relief in the iron-limitation on phytoplankton growth. The subarctic NP SEEDS-1 experiment, which was conducted under temperature conditions ideal for diatom growth (~8°C) and with shallow MLDs (~10 m), produced the greatest changes in biogeochemical parameters.

The aOIF experiments have generally led to changes in the size of the phytoplankton community from pico and nano-phytoplankton to micro-phytoplankton. This effect was particularly noticeable as diatoms became the dominant species during IronEx-2, SOIREE, EisenEx, SEEDS-1, SOFeX-S, EIFEX, and SERIES, with micro-phytoplankton accounting for ~44% of total phytoplankton community in SOFeX-N. The shift to a diatom-dominated community appears be related to the initial availability of silicate (i.e., initial silicate was >~3 μM in all the experiments just listed). Diatom-dominated blooms induced >4.5-fold increases in chlorophyll-a concentrations and accounted for >65% of the chlorophyll-a increase (Boyd et al., 2000; Gervais et al., 2002; Coale et al., 2004; Smetacek et al., 2012). However, as silicate concentrations decreased to <2 μM due to removal by the elevated diatom abundance, the extent of diatom blooms rapidly declined. In SAGE and LOHAFEX, had low initial levels of silicate (< 2 μM), pico and nano-phytoplankton dominated communities, and diatom growth was limited by the lack of available silicate. These results suggest that to develop a massive phytoplankton bloom, a changeover to a diatom-dominated community after iron addition is needed. A necessary, but not sufficient condition, for such a change to occur is the availability of silicate. Silicate alone is not expected to be sufficient because diatom-dominated blooms with distinct increases in the chlorophyll-a concentration were not observed in all experiments with high initial silicate concentrations. IronEx-1 and SEEDS-2 had high initial silicate levels (>~4 μM), which were conducive to the development of a diatom-dominated bloom, but the bloom was suppressed due to high grazing pressure. Taken together, the OIF results suggest that both mesozooplankton grazing rates as well as the initial silicate concentrations played a role in limiting the stimulation of diatom-dominated blooms after artificial iron enrichment.

In some experiments (IronEx-1, SEEDS-2, SAGE, and LOHAFEX) there was little change in the carbon export flux, while in others (IronEx-2, SOIREE, EisenEx, SEEDS-1, SOFeX-S, EIFEX, and SERIES) there was a >2-fold increase in PP within the mixed layer, with massive diatom-dominated blooms. However, even in the latter, changes in the carbon export flux differed from experiment to experiment. In SEEDS-1 and SOIREE there was little increase in export flux. However, it has been reported that changes in in the POC concentrations following an increase in PP can take three to four weeks (Buesseler et al., 2005), whereas these two experiments were conducted over only about two weeks, which suggests that the duration of each experiment was too short to detect downward carbon export. In SERIES, there was a distinct increase in the carbon export flux within the mixed layer (30 m), but there was no increase in the export flux below this because the abundance of heterotrophic bacteria was elevated after iron addition rapidly remineralized POC within the mixed layer (Boyd et al., 2004). In SOFeX-S the export flux was enhanced at 100-m depth, below the MLD (45 m). However, the changes in export flux after iron addition were not dramatic compared to natural values. It is possible that the duration of SOFeX-S was also insufficient (~4 weeks) (Table 2). EIFEX was the only aOIF experiment that produced significant carbon export to deeper layers (down to 3,000 m). This high flux was due to aggregate formation with fast sinking rates (Smetacek et al., 2012). EIFEX observed an entire cycle (i.e., development – decline – fate) of the iron-induced phytoplankton bloom during the 39 days of the experiment, which strongly suggests that a sufficient experimental duration is a prerequisite for detecting fully formed diatom aggregates (i.e., carbon export). It should also be noted that the rates of bacterial remineralization and grazing pressure on the diatoms were in the same range inside the fertilized patch as outside, which might have assisted the delivery of iron-induced POC from the MLD to the intermediate/deep depths (Smetacek et al., 2012). These results suggest that to detect significant carbon export to deep waters following an increase in PP, at least three conditions are necessary: (1) a shift to a diatom-dominated community, (2) low bacterial respiration and grazing pressure rates within the mixed layer, and (3) a sufficient experimental duration, enabling both immediate and delayed responses to iron addition to be observed.

## 3 Present: Unanswered aOIF questions - export flux, possible side effects, and international law

OIF has been proposed as a potential technique for rapidly and efficiently reducing atmospheric $CO_2$ levels at a relatively low cost (Buesseler and Boyd, 2003), but there is still much debate. Over the past 25 years, controlled aOIF experiments have shown that substantial increases in phytoplankton biomass can be stimulated in HNLC regions through iron addition, resulting in the drawdown of DIC and macronutrients (de Baar et al., 2005; Boyd et al., 2007; Smetacek et al., 2012; Martin et al., 2013). However, the impact on the net transfer of $CO_2$ from the atmosphere to the intermediate and/or deep ocean layers through the 'biological pump' is not yet fully understood or quantified and appears to vary with environmental conditions, export flux measurement techniques, and other unknown factors (Smetacek et al., 2012). While it is generally agreed that OIF effectiveness needs be determined through both tracking and quantifying export flux, there has been no discussion of which export flux measurement techniques are the most effective. In the meantime, concern has been expressed regarding possible environmental side effects in response to iron addition (Fuhrman and Capone, 1991). These side effects include the production of greenhouse gases (e.g., $N_2O$ and $CH_4$) (Lawrence, 2002; Liss et al., 2005; Law, 2008), the development of hypoxia/anoxia in the water column (Sarmiento and Orr, 1991), and toxic algal blooms (e.g., *Pseudo-nitzschia*) (Silver et al., 2010; Trick et al., 2010). Although they are accidental, these side effects could lead to negative climate and ecosystem changes (Fuhrman and Capone, 1991). Core unanswered questions remain concerning the different carbon export flux results from different measurement techniques (Boyd et al., 2002), the possible side effects that could directly influence the aOIF effectiveness, and the legal framework that is in place to protect any imprudent aOIF operations while simultaneously supporting further studies to increase our understanding of aOIF about its potential risks and benefits (Williamson et al., 2012). With the design of future aOIF experiments in mind, the following section discusses the following core questions: (1) which of the methods are optimal for tracking and quantifying carbon export flux, (2) which of the possible side effects have negative impacts on aOIF effectiveness, and (3) what are the international aOIF experimentation laws and can they be ignored?

### 3.1 Export flux measurement methods

A traditional, direct method for estimating POC export fluxes in the water column is a sediment trap that collects sinking particles (Suess, 1980). Sediment traps are generally deployed at specific depths for days to years to produce estimates of total dried mass, POC, particulate inorganic carbon (PIC), particulate organic nitrogen (PON), particulate biogenic silica (BSi), $\delta^{13}C_{org}$, and $^{234}Th$. A basic assumption for the use of a sediment trap is that it exclusively collects settling particles, resulting from the gravitational sinking of organic matter produced in surface waters. However, although they are designed to ensure the well-defined collection/conservation of sinking particles, they have accuracy issues due to: 1) interference of the hydrodynamic flow across the trap (i.e., strong advective flow), 2) inclusion/invasion (accounting for 14–90% of the total POC collected) of metazoan zooplankton (e.g., copepods, amphipods, and euphausiids) capable of vertical migration (Karl and Knauer, 1989; Buesseler et al., 1991; Buesseler et al., 2007), and 3) loss of trapped particles by bacterial decay and/or dissolution during trap deployment and storage periods (Gardner et al., 1983; Knauer et al.,1984; Kähler and Bauerfeind, 2001). The application of sediment traps for the determination of the carbon export flux is relatively more biased in the upper ocean (surface to ~1,000-m depth) where ocean currents are generally faster and zooplankton are much more active than deep water. These issues suggest that sediment traps alone may not accurately determine carbon export fluxes.

Even when used at the same depth, traditional sediment traps, such as the surface-tethered drifting trap and bottom-moored trap, can greatly over- or under-estimate particulate $^{234}Th$ fluxes compared to water-column based estimates (Buesseler et al., 1991). The water column-based total $^{234}Th$ deficiency method (the sum of dissolved and particulate activities) is less sensitive than sediment traps to the issues mentioned above, and provides better spatial and temporal resolution in flux estimates (Buesseler et al., 1998). For these reasons, traditional sediment trap POC flux estimates have often been calibrated using the total $^{234}Th$ deficiency measured using a rosette bottle or high-volume pump samples (Coale and Bruland, 1985; Buesseler et al., 2006) as a reference.

Several OIF experiments have used both sediment traps and $^{234}Th$ deficiency to estimate the iron-induced POC export flux. SOIREE reported distinct differences in POC fluxes estimated from drifting traps (185 mg $m^{-2}$ $d^{-1}$) at a 110-m depth over day 11–13 of the experiment and $^{234}Th$ (~87 mg $m^{-2}$ $d^{-1}$) at 100-m depth (Charette and Buesseler, 2000; Nodder and Waite, 2001). While there was no measurable change in $^{234}Th$-based POC fluxes during the 13 days of the SOIREE experiment (Fig. 8b), the traps suggested a 27% increase over the course of the experiment (from 146 to 185 mg $m^{-2}$ $d^{-1}$) (Table 5). It was later discovered that this increase was caused by sampling biases (Nodder et al., 2001; Nodder and Waite, 2001). Likewise, SEEDS-1 $^{234}Th$-based POC fluxes at 50-m depth over day 9–13 were estimated to be 423 mg $m^{-2}$ $d^{-1}$, but the drifting trap only recorded 141 mg $m^{-2}$ $d^{-1}$ at 40-m depth over day 12–14, 3 times lower (Table 5) (Aono et al., 2005; Aramaki et al., 2009). This large discrepancy between the two methods might be caused by the under-sampling of POC into the drifting traps (Nodder and Waite, 2001; Aono et al., 2005).

To resolve the potential biases in traditional sediment traps, a neutrally buoyant (and freely drifting) sediment trap (NBST) was developed (Valdes and Price, 2000; Valdes and Buesseler, 2006; Lampitt et al., 2008). Through preliminary experiments conducted in June and October 1997 at the Bermuda Atlantic Time-series Study site, Buesseler et al. (2000) showed that an NBST system could reduce the invasion/inclusion of zooplankton into the trap samplers, and that NBST-based $^{234}Th$ fluxes were comparable with water-column based estimates. LOHAFEX has been the only OIF experiment so far that has measured particle export using PELAGRA (Particle Export measurement using a LAGRAngian trap) sediment traps based on the NBST system (Martin et al., 2013). However, the PELAGRA sediment traps deployed below the mixed layer (at 200 m and 450 m) did not detect iron fertilization-induced carbon export even though PP did increase within the mixed layer. Water-column based $^{234}Th$ measurements estimated the POC flux at a 100-m depth to be ~94 mg $m^{-2}$ $d^{-1}$, whereas the PELAGRA sediment traps estimated the flux at 200 m and 450 m to be only ~12 mg $m^{-2}$ $d^{-1}$. It should be noted that both sediment traps and water-column based $^{234}Th$ measurements have a limited ability to fully scan the vertical profile of POC fluxes and, therefore, are of limited used in determining the fate of iron-induced POC in the water column.

To resolve the full column more effectively, LOHAFEX employed a UVP, which provided photographic evidence of sinking particles (particle size ≥100 μm) from the surface down to ~3,000-m depth, with ~0.2 m vertical resolution (Smetacek et al., 2010; Martin et al., 2013). Through an analysis of particle size distributions, the UVP also allowed particles to be classified into fecal pellets, aggregates, and live zooplankton. Vertical total particle volume profiles obtained from UVP indicated the maximum particle flux at a 75-m depth (~0.3 $mm^3$ $L^{-1}$), with a gradual decrease to 150 m (~0.15 $mm^3$ $L^{-1}$). Interestingly, large particles (i.e., zooplankton) were copious between 75-m and 100-m depth, suggesting that there might be high grazing pressure, which might explain the large discrepancy between the 100 m (water-column based $^{234}Th$ method) and 200 m / 450 m (PELAGRA sediment trap) POC flux estimates (i.e., rather than a sampling bias in sediment trap data) (Martin et al., 2013). To continuously monitor vertical changes in POC flux following iron addition, EIFEX used a transmissometer, providing high vertical resolution (~24 data points per meter) and tracking of the iron-induced flux down to ~3,000 m, even though, unlike UVPs, transmissometers do not allow classification of particles (Smetacek et al., 2012). Improving on this method, SOFeX-N applied autonomous carbon flux explorers equipped with transmissometers, designed to float along with the currents. Three autonomous carbon flux explorers were deployed, two explored the 'iron fertilized in-patch' and one acted as a 'control' outside the patch. Carbon flux explorers could continuously monitor in the field for up to 18 months beyond the initial deployment, which allowed SOFeX-N to observe 'episodic raining' in the iron-fertilized waters (Bishop et al., 2004), indicating a high carbon export flux long after artificial iron addition.

The combination of multiple approaches is essential to the successful detection of the POC produced in response to iron addition and its fate. NBST systems (e.g., the PELAGRA sediment trap) are appropriate for quantifying the aOIF-induced POC flux in the upper waters (<~400-m depth), especially when accompanied by calibration using water-column based $^{234}Th$. Particle profiling systems (e.g., a transmissometer and UVP) mounted on a CTD-Rosette sampler provide continuous quantitative and qualitative information about sinking particles, with high vertical resolution and full coverage of the water column (>3,000-m depth). They are therefore useful for indirectly identifying deep carbon transport. Autonomous carbon flux explorers are an excellent alternative, allowing the continuous observation of POC fluxes during and after an OIF experiment.

### 3.2 Considering environmental side effects

The purpose of OIF is to reduce the atmospheric $CO_2$ level by stimulating the sequestration of oceanic carbon through artificial iron additions in the HNLC regions, mitigating the global warming threat. Beyond the benefits of aOIF experimentation, scientists have debated the unintended secondary consequences of OIF, such as production of climate-relevant gases and ocean ecosystem changes. Therefore, it is important to consider the possible negative consequences of OIF to evaluate whether the aOIF experiments are effective (i.e., net profit: positives > negatives).

To investigate changes in climate-relevant gas emissions produced by biological activities and/or photochemical reactions before and after iron additions, the production of $CH_4$, $N_2O$, DMS, and halogenated volatile organic compounds (HVOCs) were measured during aOIF experiments (Liss et al., 2005), because their emission may lead to unintended consequences negating the desired effects of aOIF experiments on carbon sequestration. Among the climate-relevant gases, $CH_4$ has a ~20 times greater warming potential than $CO_2$. However, $CH_4$ has been considered to be relatively low risk because most of the $CH_4$ formed in the ocean is used as an energy source for microorganisms and is converted to $CO_2$ before reaching the sea surface (Smetacek and Naqvi, 2008; Williamson et al., 2012). During the SOFeX-N experiment, measurements of dissolved $CH_4$ indicated concentrations were slightly elevated, i.e., by less than 1% (1.74 ppmv in fertilized patch and 1.72 ppmv outside fertilized patch) (Wingenter et al., 2004). Simulated SO large-scale OIF has suggested that a 20% enhancement of $CH_4$ emissions would offset only <1% (~4 Tg C $yr^{-1}$) of the resulting carbon sequestration (Oschlies et al., 2010). Hence, additional $CH_4$ production from aOIF experiments is not likely to be a serious problem.

On the other hand, $N_2O$ has a relatively long lifetime in the atmosphere (~110 years) and has a global warming potential about 300 times greater than $CO_2$ (Forster et al., 2007). The ocean is already a significant source of atmospheric $N_2O$ (Nevison et al., 2003). Oceanic $N_2O$ is mainly produced by bacterial remineralization. Therefore, increases in $N_2O$ production after iron additions are expected and, in the long run, contribute to an increase rather than a decrease in the greenhouse effect (Bange, 2006). During the SOIREE experiment, a significant increase (~4%) in mean $N_2O$ saturation in the pycnocline (65–80 m) of the fertilized patch (104.4 ± 2.4%), as compared to outside the fertilized patch (100.3 ± 1.7%), was associated with an increased phytoplankton biomass (Law and Ling, 2001). Measurements of $N_2O$ saturation during SERIES also showed increases of 8% at 30–50 m, which were coincident with the accumulation of ammonium and nitrite attributable to increases in bacterial remineralization following increased POC levels (Boyd et al., 2004; Law, 2008). SOIREE-based model estimates suggested that potential $N_2O$ production at timescales longer than six weeks would subsequently offset carbon reduction benefits resulting from the bacterial remineralization of additional carbon fixation by 6–12% (Law and Ling, 2001). This estimate is in line with the $N_2O$ offset of 6–18% suggested by a modeling study (Jin and Gruber, 2003) and the 5–9% suggested by a more recent modeling study investigating the effectiveness of long-term and large-scale SO OIF (Oschlies et al., 2010). Excess $N_2O$ was not found after iron addition in EIFEX, where significant vertical export through the formation of rapidly sinking aggregates was found (Walter et al., 2005; Law, 2008). One explanation for the absence of $N_2O$ accumulation below the EIFEX patch might be the limited bacterial remineralization due to the rapid export of organic matter well below the 500-m depth to the seafloor (Walter et al., 2005). Based on the results of previous studies, no consensus has yet been reached on the exact extent of additional $N_2O$ production after iron additions. However, because there is the potential for excessive $N_2O$ production that would not only impact the effectiveness of aOIF experiments but also positively contribute to global warming, further studies are required to reach a conclusion.

Unlike $N_2O$ emissions, which have the potential to offset the effectiveness of OIF, DMS, a potential precursor of sulfate aerosols that cause cloud formation, may contribute to the homeostasis of the earth's climate by countering the warming due to increased $CO_2$ emissions (Charlson et al., 1987). DMS is produced by the enzymatic cleavage of planktonic dimethylsulfoniopropionate (DMSP). Microzooplankton grazing on nano-phytoplankton (e.g., haptophytes) is a key factor controlling oceanic DMS production (Dacey and Wakeham, 1986; Gall et al., 2001b; Park et al., 2014). The production of DMS in response to iron addition was measured during all aOIF experiments. In the EP and SO, DMS production increased, but in the subarctic NP, it remained constant or decreased (Lawrence, 2002; Boyd et al., 2007). There were significant short-term increases in DMS production in IronEx-2 (from 2.5 to 4.2 nM), SOIREE (from 0.5 to 3.4 nM), EisenEx (from 1.9 to 3.1 nM), and SOFeX-N (7.7 nM in the fertilized patch and 1.6 nM outside the fertilized patch) (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005; Wingenter et al., 2007). The maximum DMS production observed was a 6.8-fold increase after iron addition in SOIREE (Turner et al., 2004). During an early SOIREE experiment, the dominant phytoplankton species were haptophytes, and DMS production was increased by microzooplankton grazing on DMSP-rich haptophyte species (i.e., Prymnesiophyceae) (Gall et al., 2001b). Similarly, a 4.8-fold enhancement of DMS production was observed in SOFeX-N. Estimates derived by the extrapolation of SOFeX-N DMS production results suggested that fertilizing ~2% of the SO over the course of a week would enhance DMS production by 20%, which would lead to a 2°C decrease in air temperature over the SO (Wingenter et al., 2007). Interestingly, there were no significant changes in DMS production after iron additions in the western subarctic NP SEEDS-1/-2 experiments, despite increases in PP (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). Furthermore, in the eastern subarctic NP, SERIES DMS production increased from 8.5–10.9 nM on day 1 to a maximum of 41.2 nM on day 10, but decreased to <0.03 nM by the end of the experiment due to an increase in bacterial abundance (Table 4) (Levasseur et al., 2006). It is therefore difficult to predict the iron-induced DMS response, because OIF itself is not the only source of DMS. Based on the results of previous aOIF experiments, DMS production was sensitive in the EP and SO, but was less sensitive in the subarctic NP (Law, 2008). These results indicate that further process and modeling studies for each region are required to determine the production and degradation of DMS, both following iron fertilization and in the natural environment.

HVOCs, such as $CH_3Cl$, $CH_3Br$, and $CH_3I$, are well known for their ability to destroy ozone in the lower stratosphere and marine boundary layer (Solomon et al., 1994), and were also measured during past aOIF experiments (Wingenter et al., 2004; Liss et al., 2005). However, no consistent results have been reported for HVOCs production (Liss et al., 2005). In SOFeX-N, the impact of iron addition on HVOCs was complicated, with $CH_3Cl$ concentrations remaining unchanged, and $CH_3Br$ concentrations increasing by 14% (6.5 pptv in the fertilized patch and 5.7 pptv outside the fertilized patch), while $CH_3I$ concentrations decreased by 23% (4.9 pptv in fertilized patch and 6.4 pptv outside the fertilized patch) (Wingenter et al., 2004). In contrast, $CH_3I$ concentrations increased ~2-fold during EisenEx (Liss et al., 2005). Such a complicated response suggests that, as for DMS, further study is needed to fully understand natural cycling of HVOCs and their responses to iron fertilization.

Secondly, the effectiveness of aOIF may also be offset leading to changes in the ocean ecosystem following OIF, such as a decrease in dissolved oxygen and an increase in domoic acid (DA) levels. The decomposition of iron addition-enhanced biomass may cause decreased oxygen concentrations in subsurface waters (Williamson et al., 2012). Although mid-water oxygen depletion has not been reported from aOIF experiments to date, early modeling studies suggest that anoxic conditions may develop after long-term and large scale OIF (Sarmiento and Orr, 1991). However, more sophisticated and realistic models suggest that OIF produces well-oxygenated conditions, without the development of anoxic conditions, even under climate change scenarios (Oschlies et al., 2010; Keller et al., 2014). Thus, hypoxia/anoxia development in response to iron additions is unlikely to be a primary concern.

The changes in phytoplankton community composition after iron addition discussed in Section 2.4 may also have unintended consequences; for example, they could lead to potentially toxic species dominating plankton assemblages (Silver et al., 2010; Trick et al., 2010). Some aOIF experiments (e.g., IronEx-2, SOIREE, EisenEx, SOFeX-N/S, and SERIES) generated large blooms dominated by pennate diatoms belonging to the genus '*Pseudo-nitzschia*' (de Baar et al., 2005; Trick et al., 2010). Some '*Pseudo-nitzschia*' species have the capacity to produce the neurotoxin DA that is known to detrimentally affect marine ecosystems. However, no DA was found during EisenEx and SERIES, even though '*Pseudo-nitzschia*' were dominant (Gervais et al., 2002; Marchetti et al., 2008; Assmy et al., 2007). Phytoplankton samples used to estimate DA production had been stored for a long time before the analysis, for example, 12 years in IronEx-2 and four years in SOFeX-S (Silver et al., 2010). Trick et al. (2010) argued that phytoplankton samples stored for a long time would have degraded, leading to an under-estimation in DA production. This implies that accurate information about changes in DA production in response to iron addition might not be available. However, the IronEx-2, and SOFeX-S experiments found discernable changes in DA production, even if the original DA might have degraded (Silver et al., 2010). It is likely that several phytoplankton samples (e.g., *Pseudo-nitzschia* abundance: $1.3 \times 10^6$ cells $L^{-1}$ in IronEx-2 and $7.5 \times 10^4$ cells $L^{-1}$ in SOFeX-S) collected with a net tow were suitable to detect these changes. During IronEx-2 and SOFeX-S, high cell abundances of '*Pseudo-nitzschia*' ($10^6$ and $10^5$ cells $l^{-1}$, respectively) combined with moderate DA quotas (0.05 and 1 pg DA $cell^{-1}$, respectively) produced toxin levels as high as 45 ng DA $l^{-1}$ in IronEx-2 and 220 ng DA $l^{-1}$ in SOFeX-S, i.e., toxin levels high enough to damage marine communities in coastal waters. Therefore, it is necessary to quantify DA production in response to iron additions, with concentrated phytoplankton samples (i.e., large numbers of cells) using a net tow. This, once again, indicates that such processes need to be better understood in the natural environment before the ramifications of OIF can be fully appreciated

Whether OIF is a viable carbon removal strategy is still under debate (Boyd et al., 2007; Smetacek and Naqvi, 2008). The production of climate-relevant gases such as $N_2O$, DMS, and HVOCs, which is influenced by the remineralization of sinking particles that follows OIF-induced blooms, and the production of DA are particularly important to understand. They can directly and indirectly modify the effectiveness of carbon sequestration, with the effects being either positive or negative. Therefore, monitoring of the production of climate-relevant gases and DA to evaluate the effectiveness of OIF as a geoengineering approach is essential. This represents only a few of many possible side effects. The direct and indirect environmental consequences of OIF remain largely unresolved due to the inconsistent and highly uncertain outcomes of the experiments conducted so far, as well as our poor understanding of the processes involved under both nOIF and aOIF conditions (Chisholm et al., 2001; Johnson and Karl, 2002; Williamson et al., 2012). Therefore, considering the increasing evidence for the necessity to keep warming at or below 1.5°C (Rogelj et al., 2015), there continues to be a need to determine the effectiveness of OIF as a means for reducing atmospheric $CO_2$ through the quantification of OIF side effects.

### 3.3 Regulation of aOIF: International law of the sea as it applies to aOIF

To prevent pollution of the sea from human activities, the international Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention, 1972) was amended in 1972. In 1996, contracting parties to the London Convention adopted the Protocol to the London Convention (London Protocol, 1996). This places legal restrictions on the dumping of wastes and other matter that may cause hazard, harm, and damage in the ocean and/or interfere with the marine environment. However, the London Convention & Protocol (LC/LP) did not establish specific laws to protect the ocean environment against the side-effects of fertilization activities. In 2007, several commercial companies (e.g., GreenSea Venture [http://www.greenseaventure.com] and Climos [http://www.climos.com]) promoted large-scale (10,000 $km^2$) commercial OIF as a climate mitigation strategy and as a means to gain carbon credits (Chisholm et al., 2001; Buesseler and Boyd, 2003; Freestone and Rayfuse, 2008). Meanwhile, assessments of the effectiveness of aOIF have been limited to small fertilized patches (25–300 $km^2$) (Fig. 6a) due to the time and expense of comparing fertilized and unfertilized areas (ACE CRC, 2008). As discussed earlier, these small-area experiments have left many unanswered scientific questions regarding both the effectiveness and the potential impacts of OIF (Lawrence, 2002; Buesseler and Boyd, 2003). In the same year, noting the potential risks and benefits, the LC/LP scientific group released a statement on large-scale ocean fertilization and recommended that ocean fertilization activities be evaluated carefully to ensure that such operations were not contrary to the aims of the LC/LP.

At the 2008 LC/LP meeting, the contracting parties adopted Resolution LC-LP.1 (2008) on the regulation of ocean fertilization. This resolution prohibited ocean fertilization activities until such time that specific guidance could be developed to justify legitimate scientific research. There was an exception for ‘small-scale scientific research studies within coastal waters’ to permit the development of proposals that would lead to an assessment framework for scientific ocean fertilization research (Resolution LC-LP.1, 2008). In the meantime, there was a call to develop an assessment framework for ocean fertilization experiments to assess, accurately, scientific research proposals (Resolution LC-LP.1, 2008). In 2010, LC/LP parties developed Resolution LC-LP.2 (2010), adopting an “Assessment Framework for Scientific Research Involving Ocean Fertilization” to be used to assess, on a case-by-case basis, whether any proposed ocean fertilization activity constitutes legitimate scientific research falling within the aims and scope of Resolution LC-LP.1 (2008) (Fig. 9) (Resolution LC-LP.2, 2010). This framework demands preliminary scientific research prior to any OIF experimentation. There must be a transparent/reasonable scientific rationale/purpose to the experiment and a risk analysis must be undertaken using parameters such as problem formulation, site selection, exposure and effect assessment, and risk characterization and management. Monitoring is also required as an integral component of all approved (i.e., legitimate) scientific OIF research activity to assess ecological impacts and to review actual vs. intended geo-engineering benefits (ACE CRC, 2015). In October 2013, the LC/LP parties adopted amendments that categorize aOIF as marine geo-engineering, thereby prohibiting operational OIF activities, but enabling OIF scientific research that meets the permit conditions through the environmental assessment framework (Resolution LP.4 (8), 2013). This means that large-scale (i.e., >300 km$^2$ based on previous aOIF experiments; exact areal sizes are not determined in the LC/LP) and/or commercial OIF (e.g., 'the 2012 Haida Gwaii Iron Dump' off the west coast of Canada) are currently banned by international regulations. Under LC/LP, commercial OIF efforts cannot proceed because of the large uncertainties related to large-scale OIF.

## 4 Future: Designing future aOIF experiments

Scientific aOIF research has focused on improving our understanding of the effectiveness, capacity, and risks of OIF as an atmospheric $CO_2$ removal strategy both in the future and the past (in particular glacial periods). Although the first aOIF experiments took place more than twenty years ago, the legal and economic aspects of such a strategy in terms of the international laws of the sea and carbon offset markets are not yet clear (ACE CRC, 2015). Nonetheless, previous small-scale aOIF experiments have demonstrated a considerable potential for easily and effectively reducing atmospheric $CO_2$ levels. Accordingly, physical/biogeochemical/ecological models and nOIF experiments (long-term) have been conducted in an effort to overcome some of the limitations of short-term aOIF experiments (e.g., spatial and temporal scales) and to predict the effectiveness of long-term and large-scale fertilization (Aumont and Bopp, 2006; Blain et al., 2007; Denman, 2008; Pollard et al., 2009). For example, earlier global biogeochemical models have indicated that massive fertilization could draw down atmospheric $CO_2$ by as much as 107 μatm in 100 years (Joos et al., 1991; Peng and Broecker, 1991; Sarmiento and Orr, 1991; Kurz and Maier-Reimer, 1993). Recent global models, with more realistic ecosystem and biogeochemical cycles predict values closer to a 33 μatm drawdown in atmospheric $CO_2$ (Aumont and Bopp, 2006). These results suggest that the amount of carbon sequestration resulting from OIF represents only a modest offset, i.e., a contribution of 10% over the range of IPCC future emission scenarios (Aumont and Bopp, 2006; Denman, 2008). The nOIF experiments have also produced much higher carbon sequestration rates than the small-scale aOIF experiments (Morris and Charette, 2013). Furthermore, the results from nOIF experiments do not support the potential negative impacts proposed for OIF experiments, even at larger scales (Belviso et al., 2008). However, these nOIF results do not guarantee that aOIF as a geoengineering approach is able to achieve the high effectiveness associated with carbon sequestration and enables a simple scaling-up as a prediction tool, because the nOIF experiments differ from the aOIF experiments in the mode of iron supply. In particular, nOIF is a continuous and slow process and its iron source is based on the upwelling of iron-rich subsurface waters to the surface layer, whereas aOIF is intended to be episodic, with massive short-term iron additions (Blain et al., 2007). In addition, in nOIF it is difficult to accurately identify iron sources due to the complexity of the system, whereas in aOIF there is quantitative and qualitative information about iron additions and sources (Blain et al., 2008). Contrary to the results of aOIF experiments in the SO (e.g., SOIREE and SOFeX-N), no increase in DMS emissions was found in nOIF experiments in the SO (i.e., Kerguelen Ocean and Plateau compared Study: KEOPS) (Belviso et al., 2008), suggesting that it might be difficult to identify the potential long-term negative effects of aOIF by studying the naturally fertilized systems in the SO. Therefore, it is important to continue undertaking small-scale studies to obtain a better understanding of natural processes in the SO as well as to assess the associated risks, and so lay the groundwork for evaluating the potential effectiveness and impacts of large-scale OIF as a geoengineering solution to anthropogenic climate change. It is therefore of paramount importance that future aOIF experiments continue to focus on the effectiveness and capacity of aOIF as a means of reducing atmospheric $CO_2$, but they should also carefully consider the location (i.e., 'where'), timing (i.e., 'when'), and duration (i.e., 'how long'), as well as modes of iron addition (i.e., 'how'), tracing methods/parameters measurements/protocols (i.e., 'what'), and side effects on marine/ocean ecosystems (i.e., 'what concerns'). This will build on the results of previous aOIF experiments, develop our understanding of the magnitude and sources of uncertainties, and provide confidence in our ability to reproduce results.

Where: The first consideration for a successful aOIF experiment is the location. The dominance of diatoms in phytoplankton communities plays a major role in increasing the biological pump because diatom species can sink rapidly as aggregates or by forming resting spores (Tréguer et al., 1995). Previous aOIF experiments have shown that silicate concentration is the crucial factor inducing diatom blooms. Therefore, to obtain the greatest possible carbon export flux in response to iron addition, aOIF experiments should be designed in regions with high silicate concentrations, such as in the subarctic NP (e.g., SEEDS-1 experiment) and the south of PF of the SO (e.g., SOFeX-S experiment) >~15 μM (Fig. 4c). In selecting sites for iron fertilization, it is also important to distinguish the iron-fertilized patch from the surrounding unfertilized waters to observe, easily and efficiently, iron-induced changes (Coale et al., 1996). Ocean eddies provide an excellent setting for aOIF experimentation because they tend to naturally isolate interior waters from the surrounding waters. Mesoscale eddies range from 25–250 km in diameter and maintain their characteristics for 10–100 days after formation (Morrow and Le Traon, 2012; Faghmous et al., 2015). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds, with low shear and high vertical coherence, providing ideal conditions for tracing the same water column from the surface to the deep layers, as well as minimizing lateral stirring and advection (Smetacek et al, 2012). Therefore, finding an appropriate eddy setting in a study area should be a high priority consideration when conducting an aOIF experiment (Smetacek and Naqvi, 2008).

When: The second consideration for a successful aOIF experiment is timing, which includes when an experiment starts. PP in ocean environment is generally limited by nutrient availability and/or by light availability, often referred to as a single- or co-limitation. PP in the SO, a representative HNLC region, is subject to co-limitation by micro/macro-nutrients (i.e., iron and/or silicate) and light availability (Mitchell et al., 1991). In the south PF of SO, phytoplankton blooms usually occur during the early summer (i.e., from late December to early January) due to the increasing nutrient flux from the subsurface waters to the surface waters by the shoaling of MLD, along with the receipt of sufficient solar radiation (Moore and Abbott, 2002). Prior to December, phytoplankton growth is mainly limited due to light availability (Mitchell et al., 1991; Veth et al., 1997; Abbott et al., 2000), while after January (i.e., during late summer and early autumn from February to March) it is mainly limited due to silicate availability. In previous aOIF experiments in the SO that have been conducted between spring and early autumn, PP was mainly limited by iron and/or silicate availability rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011). In addition, the grazing pressure of mesozooplankton (i.e., copepods) on large diatoms was also a major limiting factor in diatom production (Coale et al., 2004; Martin et al., 2013), and was generally higher during late summer and early autumn (February to March) (Le Quéré et al., 2016). Considering the key factors (i.e., micro/macro nutrient availability, light availability, and grazing pressure) controlling PP in the SO, the most appropriate timing for an aOIF experiment to start in the SO is likely to be the early summertime (i.e., late December to early January).

How long: The third consideration for a successful aOIF experiment is the duration. Although the periods that phytoplankton blooms have been maintained by OIF have lasted from ~10 to ~40 days (Kolber et al., 1994; Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012), it has also been suggested that most aOIF experiments did not cover the full response times from onset to termination (Boyd et al., 2005). For example, SOIREE and SEEDS-1 had relatively short observation periods (13 days) and saw increasing trends in PP throughout the experiments (Fig. 10a), suggesting that the observation period should have been extended. Furthermore, after the end of SOIREE, ocean color satellite images showed continued high chlorophyll-a concentrations (>1 mg $m^{-3}$) in the iron fertilized patch, which was visible as a long ribbon shape that extended some 150 km for >40 days (~6 weeks) after the initial iron addition (Fig. 10b) (Abraham et al., 2000; Westberry et al., 2013). This indicates that short experimental durations may not be sufficient for detecting the full influence of artificial iron additions on PP and ecosystem (Figs. 8b and 10) (Boyd et al., 2000; Tsuda et al., 2003; de Baar et al., 2005). SOFeX-S also resulted in relatively low export production despite the high PP due to the experimental duration being insufficient to cover the termination of the phytoplankton bloom. However, SERIES, SEEDS-2, EIFEX, and LOHAFEX did fully monitor all phases of the phytoplankton bloom from onset to termination. EIFEX, the third-longest aOIF experiment, at 39 days, was the only one that observed iron-induced deep export production between day 28 and 32 (Table 5 and Fig. 8a) (Smetacek et al., 2012; Assmy et al., 2013). Furthermore, long-term observations covering the later stage of bloom development during nOIF experiments resulted in much higher Fe:C export efficiencies compared to the short-term aOIF (Blain et al., 2007; Pollard et al., 2009). Based on previous aOIF experiments, it would, therefore, be important to detect the full phase of a phytoplankton bloom to determine accurately the amount of iron-induced POC exported out of the mixed layer. The observation period is, therefore, an important factor to consider in budget and effectiveness estimates. It is suggested that the experimental duration should be a minimum of ~40 days based on the SOIREE experiment, which produced the longest iron-induced bloom (i.e., the longevity of >40 days).

How: The fourth consideration for a successful aOIF experiment lies in the strategy/approach of adding and maintaining dissolved iron within the upper mixed layer to produce a phytoplankton bloom. First, the chemical form for iron addition should be acidified iron-sulfate, which is less expensive and more bioavailable than other iron compounds. The amount of iron-sulfate required is calculated according to the target concentration of the dissolved iron and volume (MLD × patch size). Based on bottle incubation experiments, target iron concentrations of ~2–4 nM are recommended to stimulate maximum phytoplankton growth due to the rapid losses of added iron by horizontal advection/diffusion and oxidation to poorly bioavailable iron(III) (Coale et al., 1996; Coale et al., 1998; Bowie et al., 2001). For patch size, a biogeochemical model study showed that a fertilized patch size of 156 $km^2$ maintained an iron concentration above 0.3 nM for 56 days, while a longer period of 194 days required a fertilized patch size of 160,000 $km^2$ (Xiu and Chai, 2010). This is because, compared to larger iron-fertilized patches, a smaller patch size tended to lose iron more rapidly due to dilution effects with unfertilized water. Previous aOIF experiments also produced similar results to this model study. The lateral dilution rate (<0.25 $d^{-1}$) during SAGE, which had the smallest fertilized patch size (36 $km^2$) of the SO experiments, was two times higher than the rates (<0.11 $d^{-1}$) in the SO experiments with a larger fertilized patch size (e.g., EIFEX fertilized with a patch size of 167 $km^2$ and SOFeX-N/S fertilized with a patch size of 225 $km^2$) (Coale et al., 2004; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012). Therefore, it would be more appropriate to fertilize a large area (e.g., LOHAFEX had the largest aOIF experiment at 300 $km^2$), which would reduce the dilution effect with unfertilized waters (Xiu and Chai, 2010). Based on a ~2 nM iron concentration for a patch size of 300 $km^2$ and MLD of ~60 m, it would need ~2,000 kg of iron(II) to be applied in a fertilization experiment. Iron should be released into the wake of a ship, with the release track describing an expanding spiral (or square) in the eddy center, with a regular interval of ~1 km throughout the patch, because it is easier to locate a fertilized patch than a point release (Watson et al., 1991). In addition, it should be completed within ~24 hours because of the time-dependent phytoplankton response within the iron-fertilized patch. Previous aOIF experiments have shown that multiple iron additions (≥2 infusions) are needed to maintain the dissolved iron concentration required to derive maximum phytoplankton growth within the fertilized patch. For example, in SOIREE it was found that four additions of iron at intervals of about three days led to persistently high levels of both dissolved and particulate iron within the mixed layer, with a rapid reduction at the end of the experiment, combined with an increase in the concentration of iron-binding ligands (Bowie et al., 2001). In both EIFEX and SOFeX-S, it was also found that multiple iron(II) infusions (in particular, two infusions with intervals of 13 days in EIFEX and four infusions with intervals of four days in SOFeX-S) allowed iron to persist in the mixed layer longer than its expected oxidation kinetics. The relatively low oxidation rates were related to a combination of photochemical production, slow oxidation and, possibly, organic complexation (Croot et al., 2008). Blain et al. (2007) explained that the higher carbon sequestration effectiveness of nOIF experiments compared to aOIF experiments partly resulted from the slow and continuous iron addition that occurs in the natural environment. Large amounts of iron addition at one time can lead to a substantial loss of artificially added iron. Therefore, for an experimental duration of >~40 days, a minimum of three iron infusions at intervals of ~10–15 days would be required to prevent the iron limitation on phytoplankton growth, based on the EisenEx and EIFEX experiments (Nishioka et al., 2005; Smetacek et al., 2012).

What: The fifth consideration for a successful aOIF experiment is the effective tracing of the fertilized patch, including the detection of carbon sequestration (Buesseler and Boyd, 2003). All previous aOIF experiments used physical tracers, in particular GPS and ARGO equipped drifting buoys, to follow the iron fertilized patch. A drifting buoy is a natural and passive system moving along with the currents, but it can be escaped from the fertilized patch due to the action of strong winds (Tsumune et al., 2005). Therefore, the release of GPS and ARGO equipped drifting buoys at the center of the patch after the iron infusions would provide a visual map showing the tracked positions of the fertilized patch. An inert chemical tracer, such as $SF_6$, would also be an excellent option for following the fertilized patch after iron addition. Previous aOIF experiments have shown that the $SF_6$ measurements based on underway sampling systems can be used to determine accurately time-dependent vertical and lateral transport of iron-fertilized patches. Many subsequent aOIF experiments have also used tracing methods based on the observation of biogeochemical parameters (such as the Fv/Fm ratio, chlorophyll fluorescence, and underway $pCO_2$) before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Coale et al., 2004; Boyd et al., 2004; Tsuda et al., 2005; Smetacek et al., 2012). The Fv/Fm ratio can be easily and promptly used as an indicator to track the fertilized patch due to its rapid response to iron addition. Direct measurements of carbon export fluxes to determine the effectiveness of aOIF should be conducted by deploying an NBST at two depths: (1) within the mixed layer to detect increases in iron-induced POC in the surface layer along with the calibration of a water-column based $^{234}$Th method, and (2) below the depth of the winter MLD to detect iron-induced export carbon fluxes into intermediate/deeper waters (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Buesseler et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). Sinking-particle profiling systems mounted on autonomous floats, such as a transmissometer and UVP that measure and photograph sinking particles, could provide a record of the temporal and vertical evolution of iron-induced POC stocks through successive depth layers down to ~3,000-m depth for ~20 months after deployment, once calibrated using POC fluxes measured from sediment traps and/or a water-column based $^{234}$Th method (Bishop et al., 2004; Smetacek et al., 2012; Martin et al., 2013). Future OIF experiments would benefit from these technological advances, enabling a more efficient tracing of the carbon export flux and particle size and composition at higher vertical and temporal resolution than has been possible in the past. Hence, the application of an NBST system and water-column based $^{234}$Th method to direct flux estimates, combined with autonomous sinking-particle profilers of a transmissometer and UVP, will enable the quantitative and qualitative evaluation of the effectiveness of aOIF and direct observation of iron-induced carbon export fluxes after artificial iron additions.

What concerns: The sixth consideration for a successful aOIF experiment is the monitoring of possible side effects. The LC/LP parties recently adopted Resolution LC-LP.2 (2010), which includes the "Assessment Framework for Scientific Research Involving Ocean Fertilization". This considers possible side effects on marine/ocean ecosystems after artificial iron additions, such as the production of climate-relevant gases and negative ecosystem changes, which are vital to assess when proposing an aOIF experiment. The emissions of climate-relevant gases, such as $N_2O$, DMS, and HVOCs, may directly contribute to warming or cooling effects, and toxic DA production may have a negative impact on marine/ocean ecosystems (Law, 2008; Silver et al., 2010; Trick et al., 2010), resulting in significant offsets against the benefits of aOIF experiments. However, there is little quantitative and qualitative information regarding possible side effects following the previous aOIF experiments. Therefore, the future monitoring of these potential side effects is a prerequisite to evaluate accurately the effectiveness of an aOIF experiment in the future.

In summary, to maximize the effectiveness of aOIF experiments in the future, we suggest a design that incorporates several conditions. (1) Experiments are conducted in the center of an eddy structure when grazing pressure is low and silicate levels are high (e.g., in the case of SO, at the south of PF during the early summer). (2) Shipboard observations are made during a minimum of ~40 days, with multiple iron injections (iron infusions of ~2,000 kg at least three times, with an interval of ~10–15 days, to fertilize a patch of 300 $km^2$ to obtain a ~2 nM concentration). (3) The iron-fertilized patch is traced using both physical (e.g., a drifting buoy) and biogeochemical (e.g., $SF_6$ and the Fv/Fm ratio) tracers. (4) NBST system and water-column derived $^{234}Th$ method are employed at two depths (one within the mixed layer and another below it), with autonomous profilers equipped with UVP and transmissometers to estimate accurately the carbon export flux. (5) The side effects on marine/ocean ecosystems are monitored, including the production of climate-relevant gases (e.g., $N_2O$, DMS, and HVOCs) and toxic DA.

## 5. Design of the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES)

### 5.1 Background - Bransfield Basin

A science-oriented aOIF project, KIFES (Fig. 11), was launched in 2016 with research funding from the Korean Ministry of Oceans and Fisheries. This project was largely managed by the Korea Polar Research Institute (KOPRI) with domestic collaborators (i.e., Incheon National University, Inha University, Pusan National University, Hanyang University, and Yeonsei University) and strengthened by international collaborators (i.e., Alfred-Wegener-Institut (AWI), Institute of Geological and Nuclear Sciences, Massachusetts Institute of Technology Woods Hole Oceanographic Institution (MIT-WHOI), University of Otago, University of California at Irvine, McMaster University, University of South Florida, Royal Netherlands Institute for Sea Research, and Dalhousie University). KIFES had four main aims. (1) To conduct the first scientific aOIF experiment complying with the “Assessment Framework for Scientific Research Involving Ocean Fertilization” after the framework was accepted from the LC/LP in 2010. (2) To evaluate the effectiveness of scientific aOIF in terms of atmospheric carbon sequestration (i.e., to identify/quantify significant increases in iron-induced carbon export fluxes into intermediate/deeper waters) in the SO. (3) To determine the environmental conditions that would maximize the effectiveness of aOIF. (4) To quantitatively and qualitatively monitor short- and long-term possible side effects derived from previous aOIF experiments.

A location near the eastern Bransfield Basin was considered for the site of KIFES based on the following three criteria: (1) the possibility of diatom blooms, (2) the proximity to meso-scale eddies, and (3) the availability of historical oceanographic data. The development of a diatom bloom is the first prerequisite to maximize the effectiveness of an aOIF experiment. The paleoclimate team at KOPRI had found geological evidence of massive amounts of organic carbon buried in the sediments, especially in the diatomaceous ooze layer, in the eastern Bransfield Basin on the Antarctic Peninsula (Yoo et al., 2016). The well-preserved diatomaceous ooze layer (Bahk et al., 2003; Kang et al., 2003; Bak et al., 2015) indicates high accumulation rates of fast sinking diatoms, suggesting the existence of a strong ‘biological pump (i.e., significant export production)’ in this basin. In addition, this basin has a high silicate concentration of ~30 μM (Fig. 4c), which is a fundamental condition to produce a massive diatom bloom. Despite the favorable environmental conditions, the Fv/Fm ratio in/near the eastern Bransfield Basin (<~0.43) (Park et al., 2013) was lower than the maximum value of 0.65 measured during the aOIF experiments in the SO (e.g., SOIREE and SOFeX-S), suggesting an iron limitation on diatom growth. Therefore, we hypothesized that the input of bioavailable iron enabling an increase in productivity and export would lead to a massive enhancement of the diatom flux in this basin. Accordingly, we expected that an aOIF in the diatom-dominated region with high sinking rates near the eastern Bransfield Basin would be more effective for carbon export, as compared to the previous aOIF experiments conducted in the SO. This hypothesis, based on sedimentary evidence, was not considered in the site selection for previous experiments. A second important factor was the presence of stable eddies in/near the eastern Bransfield Basin (Kahru et al., 2007; Sangrà et al., 2011), providing coherent structures that made it possible to track effectively the iron-induced carbon export fluxes (Smetacek et al., 2012). For example, Thompson et al. (2009) showed that a large standing eddy (~40 km in diameter) was centered at ~62°S and 54°W and remained for ~30 days using historical drifters released during the period 1989–2005, and 40 drifters released in February 2007 as part of the Antarctic Drifter Experiment: Links to Isobaths and Ecosystems project. Satellite sea-level height images have indicated meso-scale eddies with long lifespans in/near the eastern Bransfield Basin (https://www.aviso.altimetry.fr/). Additionally, several historical oceanographic datasets are available for this basin (Grelowski et al., 1986; Helbling et al., 1995; Figueiras et al., 1999; Kang et al., 2001; Varela et al., 2002; Khim et al., 2005). The historical datasets provide general oceanographic characteristics about sites for an aOIF experiment as well as basic information helpful for designing the experiment, including a preliminary hydrographic survey. Unfortunately, KIFES has lost its source of funding. Nevertheless, optimism prevails that alternative funding will be found at a future date and the following section is intended, therefore, to provide a basic set of design guidelines, with the expectation that an opportunity to move forward with KIFES will occur in the near future.

## 5.2 A plan for the future: KIFES

The KIFES design entails a five-year project plan modeled on the 'EIFEX' program that found deep carbon by conducting an aOIF experiment in the center of an eddy structure. The KIFES project would include a preliminary environmental survey both outside and inside the center of an eddy structure formed in/near the eastern Bransfield Basin, a scientific aOIF experiment, and an assessment of the full KIFES project. In this section, we introduce the major goals, objectives, and main tasks of KIFES.

### 5.2.1 Year one plan

Goals: (1) Data collection with regard to oceanographic conditions in/near the eastern Bransfield Basin, including both eddy development and distribution. (2) Establishment of the study aims, hypothesis, and site for the KIFES experiment.

Objective: To understand the physical and biogeochemical oceanography of relevance to the eastern Bransfield Basin as an OIF site through an analysis of earlier datasets and a review of published papers.

Main tasks: (1) Review databases of physical and biogeochemical parameters from previous surveys conducted in/near the eastern Bransfield Basin. (2) Review the eastern Bransfield Basin oceanographic conditions using data analysis and references. (3) Establish the study aims, hypothesis, and site in/near the eastern Bransfield Basin for an aOIF experiment, based on the results obtained from tasks (1) and (2). (4) Design an oceanographic cruise map for the first preliminary survey in/near the eastern Bransfield Basin. (5) Analyze eddy development and distribution using satellite data in/near the eastern Bransfield Basin. (6) Prepare scientific instruments for ocean physical and biogeochemical monitoring. (7) Establish an international collaborative OIF network. (8) Submit KIFES field program proposal for the 'Initial Assessment' to determine that KIFES falls within the remit of ocean fertilization and should be evaluated in the LC/LP assessment framework based on the results from tasks (1) and (2).

**5.2.2 Year two plan**

Goal: First preliminary hydrographic survey to provide a foundational understanding of oceanographic conditions in/near the eastern Bransfield Basin.

Objectives: (1) To obtain information about oceanographic conditions from *in situ* measurements in/near the eastern Bransfield Basin. (2) To provide background information before the KIFES experiment.

Main tasks: (1) Using the ice breaker RV *ARAON*, undertake a field investigation in/near the eastern Bransfield Basin to determine physical and biogeochemical parameters associated with both carbon sequestration and OIF side effects (e.g., production of $N_2O$, DMS, HVOCs, and DA), based on the first-year results. (2) Prepare an 'Environmental Assessment' for the LC/LP assessment framework based on the first-year results and a preliminary hydrographic survey.

**5.2.3 Year three plan**

Goals: (1) Preliminary hydrographic survey outside/inside the center of an eddy structure prior to the KIFES experiment. (2) Approval of KIFES from LC/LP.

Objectives: (1) To compare oceanographic conditions inside and outside the center of an eddy structure formed in/near the eastern Bransfield Basin prior to the KIFES experiment. (2) To obtain a permission on the basis that the proposed KIFES is legitimate scientific research from the LC/LP.

Main tasks: (1) Using the ice breaker RV *ARAON*, detect an eddy formed in/near the eastern Bransfield Basin using observations from acoustic Doppler current profilers (ADCPs) and satellites. (2) Conduct intensive physical and biogeochemical field investigations both inside and outside the center of an eddy structure. (3) Assess the physical and biogeochemical properties outside vs. inside the center of an eddy structure prior to KIFES. (4) Establish a final design for KIFES. (5) Submit the research results for 'Environmental Assessment' stage of the LC/LP assessment framework and obtain approval for the KIFES experiment via the 'Decision Making' process from the LC/LP.

**5.2.4 Year four plan**

Goal: Conduction of the KIFES scientific aOIF experiment in the center of an eddy structure during the early summertime (Fig. 11).

Objective: To conduct a scientific aOIF experiment in the center of an eddy structure formed near/in the eastern Bransfield Basin.

Main tasks: (1) Using the ice breaker RV *ARAON*, detect an eddy formed in/near the eastern Bransfield Basin using observations from ADCPs and satellites, and investigate the initial environmental conditions for ~4 days before KIFES. (2) Execute the KIFES field campaign during a >~40-day period with the eddy structure. (3) At least three iron additions at intervals of ~15 days, with each iron injection being ~2,000 kg following a spiral ship track, with a regular interval of ~1 km to create a patch size of 300 $km^2$ (target dissolved iron concentration of ~2 nM). (4) Trace the fertilized patch with deployments of GPS and ARGO equipped drifting buoys, biogeochemical tracers ($SF_6$ and Fv/Fm ratio) employing underway-sampling systems, and gliders equipped with biogeochemical sensors. (5) Measure iron-induced carbon export fluxes for the regions both inside and outside the center of an eddy structure using NBST systems at two depths (one within the mixed layer and another below it) along with the calibration of water-column based $^{234}Th$ measurements and autonomous profilers equipped with transmissometer and UVP. (6) Monitor possible side effects, such as the production of climate-relevant gases and toxic DA. (7) Monitor continued responses after KIFES termination using satellite observations and autonomous profilers. (8) Assess the effectiveness of carbon sequestration and environmental (ocean and atmosphere) side effects for KIFES and prepare the KIFES assessment for the 'Results of Monitoring' stage of the LC/LP assessment framework.

#### 5.2.5 Year five plan

Goal: Integrated assessment of the KIFES project.

Objective: To evaluate whether small-scale scientific aOIF experimentation can be an effective tool for detecting the effectiveness of artificially iron-induced export production and determining any negative impacts on climate change.

Main tasks: (1) Submit the KIFES assessment report. (2) Submit scientific results to international journals. (3) Collect feedback regarding the KIFES project from international scientific/oceanographic communities. (4) Produce a final aOIF experimental summary (including main tasks (1)–(3)). (5) Submit a final report of the KIFES assessment to the LC/LP.

### 5.3 Final Remark

None of the KIFES scientists have commercial interests (i.e., carbon credits) related to aOIF experiments. The interests of KIFES participants all lie in the detailed investigation of the biogeochemical effects of scientific artificial iron addition in the SO and in OIF as a possible geo-engineering method to mitigate the climate change effects we will face in the future. We envisage a future where the KIFES, or similar projects, can be resumed, enabling a more robust assessment of the potential of OIF as a geo-engineering solution to help reduce atmospheric $CO_2$ concentrations. A continuation of the KIFES project would provide fundamental information and guidelines for future scientific aOIF experiments in HNLC regions, as well as improving our understanding of SO biogeochemistry. The risks and side effects of aOIF should be thoroughly investigated to calm international concerns. Finally, we emphasize that international cooperation is essential for a project as organizationally and scientifically complex as KIFES, and that we seek to improve our knowledge and provide a positive outlook for the Earth's future.

## 6 Summary

To test Martin's hypothesis, a total of 13 scientific aOIF experiments have been conducted in HNLC regions during the last 25 years. These aOIF experiments have resulted in increases of PP and drawdowns of macro-nutrients and DIC. In most experiments, the phytoplankton group has tended to shift from small-sized to large-sized plankton cells (mostly diatom-dominated). However, their effectiveness in enhancing export production has not been confirmed, except for EIFEX. Likewise, the possible environmental negative side effects in response to iron addition, such as the production of climate-relevant gases and toxic DA, could not be fully evaluated due to the widely differing outcomes, with large uncertainties depending on OIF experimental conditions and settings. In particular, the monitoring of $N_2O$, DMS, and HVOCs is essential to determine the effectiveness of OIF as a geoengineering approach, because these potential trace gas emissions can directly and indirectly modify the carbon reduction benefits resulting from OIF. Furthermore, toxic DA production may cause serious damage to marine/ocean ecosystems. Therefore, the validation and suitability of aOIF for the mitigation of rapidly increasing atmospheric $CO_2$ levels is a subject of vigorous debate. At present, large-scale and/or commercial aOIF is prohibited by international regulation, while small-scale aOIF experimentation for scientific purposes is permitted. To maximize the effectiveness of aOIF, future aOIF experiments should be conducted by carefully considering the major factors including the methods for iron addition, tracking methods, measurement parameters, location, timing, and experimental duration, under international aOIF regulations. Finally, we envisage a future where the KIFES project, or a similar alternative, becomes a reality so that we may determine whether OIF is a promising geo-engineering solution.

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**Table 1.** Summary of ocean iron fertilization (OIF) experiments; time, location, research vessel, added iron(Ⅱ) (values in brackets correspond to the number of days from the first iron addition, e.g., the first iron addition becomes (0)), initial iron concentrations, after iron addition concentrations (iron concentrations after iron addition), tracer, initial patch size, experiment duration, and regional characteristics (HNLC: high-nutrient and low chlorophyll).

| | Experiment | Time | Location | Research vessel | Added iron(Ⅱ) (kg) (day) | Initial iron (nM) | After iron addition (nM) | Tracer | Patch size ($km^2$) | Duration (days) | Regional characteristics |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | Oct 1993 | Equatorial Pacific<br>5° S, 90° W | RV *Columbus Iselin* | ①450 (0) | 0.06 | 3.60 | $SF_6$ | 64 | 10 | HNLC |
| 2 | IronEx-2 | May 1995 | Equatorial Pacific<br>3.5° S, 104° W | RV *Melville* | ①225 (0)<br>②112 (3)<br>③112 (7) | 0.02 | 2.00<br>1.00<br>1.00 | $SF_6$ | 72 | 17 | HNLC |
| 3 | SOIREE | Feb 1999 | Southern Ocean-Australasian-Pacific sector<br>61° S, 140° E | RV *Astrolab* | ①768 (0)<br>②312 (3)<br>③312 (5)<br>④353 (7) | 0.08 | 3.80<br>2.60<br>2.60<br>2.50 | $SF_6$ | 50 | 13 | HNLC |
| 4 | EisenEx | Nov 2000 | Southern Ocean-Atlantic sector<br>48° S, 21° E | RV *Polarstern* | ①780 (0)<br>②780 (7)<br>③780 (16) | 0.06 | 2.00 | $SF_6$ | 50 | 23 | HNLC |
| 5 | SOFeX-N | Jan–Feb 2002 | Southern Ocean-Pacific sector<br>56.23° S, 172° W | RV *Revelle*<br>RV *Melville* | ①631 (0)<br>②631 (4)<br>③450 (29) | | 1.20<br>1.20<br>1.50 | $SF_6$ | 225 | 40 | *HNLCLSi |
| 6 | SOFeX-S | Jan–Feb 2002 | Southern Ocean-Pacific sector<br>66.45° S, 171.8° W | RV *Revelle*<br>RV *Melville*<br>RV *Polar star* | ①315 (0)<br>②315 (5)<br>③315 (8)<br>④315 (12) | | 0.70<br>0.70<br>0.70<br>0.70 | $SF_6$ | 225 | 28 | HNLC |
| 7 | EIFEX | Feb–Mar 2004 | Southern Ocean-Atlantic sector<br>50° S, 2° E | RV *Polarstern* | ①1410 (0)<br>②1410 (13) | 0.20 | 1.50<br>0.34 | | 167 | 39 | HNLC |

To be continued

| - | Experiment | Time | Location | Research vessel | Added iron(Ⅱ) (kg) (day) | Initial iron (nM) | After iron addition (nM) | Tracer | Patch size ($km^2$) | Duration (days) | Regional characteristics |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | SAGE | Mar–Apr 2004 | Southern Ocean- Southeast of New Zealand 46.5° S 172.5° E | RV *Tangaroa* | ①265 (0) ②265 (6) ③265 (9) ④265 (12) | 0.09 | 3.03 1.59 0.55 1.01 | $SF_6$ | 36 | 15 | *HNLCLSi |
| 9 | LOHAFEX | Jan–Mar 2009 | Southern Ocean- Atlantic sector 48° S, 15° W | RV *Polarstern* | ①2000 (0) ②2000 (18) | | 2.00 | $SF_6$ | 300 | 40 | *HNLCLSi |
| 10 | SEEDS-1 | Jul–Aug 2001 | Subarctic North Pacific- Western basin 48.5° N, 165° E | RV *Kaiyo-Maru* | ①350 (0) | 0.05 | 2.90 | $SF_6$ | 80 | 13 | HNLC |
| 11 | SERIES | Jul-Aug 2002 | Subarctic North Pacific- Eastern basin 50.14° N, 144.75° W | RV *John P. Tully* RV *El Puma* RV *Kaiyo Maru* | ①245 (0) ②245 (6) | <0.10 | 2.00 0.60 | $SF_6$ | 77 | 25 | HNLC |
| 12 | SEEDS-2 | Jul–Aug 2004 | Subarctic North Pacific- Western basin 48° N, 166° E | RV *Hakuho-Maru* RV *Kilo-Moana* | ①332 (0) ②159 (6) | 0.17 | 1.38 | $SF_6$ | 64 | 26 | HNLC |
| 13 | FeeP | Apr–May 2004 | Subtropical North Atlantic- North-east Atlantic 27.5° N 22.5° W | RV *Charles Darwin* RV *Poseidon* | ①1840 (0) | 0.20–0.40 | 3.00 | $SF_6$ | 25 | 21 | LNLC |
| I | **CROZEX | Nov 2004– Jan 2005 | Southern Ocean- South of sub-Antarctic Front 44° S, 50° E | RV *Discovery* | _ | | 0.55 | | _ | _ | HNLC |
| II | **KEOPS | Jan–Feb 2005 | Southern Ocean- South of Polar Front 50° S, 73° E | RV *Marion Dufresne* | _ | 0.09 | 0.35 | | _ | _ | HNLC |

*High Nutrient Low Chlorophyll and Low Silicate (HNLCLSi) region; **natural OIF experiments (CROZet natural iron bloom and EXport experiment: CROZEX; KErguelen Ocean and Plateau compared Study: KEOPS).

Sources are Martin et al. (1994); Coale et al. (1996); Coale et al. (1998); Boyd et al. (2000); Boyd and Law (2001); Gervais et al. (2002); Tsuda et al. (2003); Boyd et al. (2004); Coale et al. (2004); Bakker et al. (2005); Boyd et al. (2005); de Baar et al. (2005); Nishioka et al. (2005); Hoffmann et al. (2006); Law et al. (2006); Blain et al. (2007); Boyd et al. (2007); Rees et al. (2007); Tsuda et al. (2007); Pollard et al. (2009); Strong et al. (2009); Harvey et al. (2010); Smetacek et al. (2012); and Martin et al. (2013).

**Table 2.** Summary of artificial ocean iron fertilization (aOIF) experiments; objectives, significant results, and limitations.

| | Experiment | Objectives | Significant results | Limitations |
|---|---|---|---|---|
| 1 | IronEx-1 | • To test the hypothesis that artificial iron addition will increase phytoplankton productivity by relieving the iron limitation of phytoplankton in high-nutrient low chlorophyll regions | • Small increases in the Fv/Fm ratio, chlorophyll-a concentration, and primary production (PP)<br>• Insignificant changes in nutrients and $pCO_2$ concentrations | • Single iron addition<br>• Insufficient experimental periods to observe the full phases of biogeochemical responses from the onset to termination after iron additions<br>• Micro/macro-nutrient limitations |
| 2 | IronEx-2 | • To test three hypotheses that were advanced to explain the weak biogeochemical response observed during IronEx-1 | • Dramatic changes in biogeochemical responses; close to support for Martin's hypothesis<br>• Taxonomic shift toward diatom-dominated phytoplankton communities | • No export flux measurements in the deep ocean<br>• Insufficient experimental duration |
| 3 | SOIREE | • To test the iron hypothesis in the Southern Ocean | • Diatom-dominated bloom<br>• No measurable change in carbon export | • Insufficient experimental duration |
| 4 | EisenEx | • To test the hypothesis that atmospheric dust inputs might have led to a dramatic increase in ocean productivity during the Last Glacial Maximum due to the relief of iron-limited conditions for phytoplankton growth | • Diatom-dominated bloom<br>• No clear differences in carbon flux between in-patch and outside-patch | • Light limitation by storms<br>• Insufficient experimental duration |
| 5 | SOFeX-N | • To address the potential for iron and silicate interactions to regulate the diatom bloom | • Remarkable increase in diatom biomass<br>• Observation of large export flux event with transmissometers | • Entrainment of dissolved silicate into the fertilized patch by physical mixing<br>• No direct measurement of export fluxes with sediment traps |
| 6 | SOFeX-S | • To address the potential for iron and silicate interactions to regulate the diatom bloom | • Significantly enhanced export fluxes out of the mixed layer, but similar to those for natural blooms | • Insufficient experimental duration |
| 7 | EIFEX | • To confirm that aOIF experiments can increase export production | • Observation of all the phases of the phytoplankton bloom from onset to termination<br>• Significant carbon export to deeper layers (down to 3,000 m) due to the formation of aggregates with rapid sinking rates<br>• The occurrence of rapidly sinking large aggregates | |

To be continued

| | Experiment | Objective | Significant results | Limitations |
|---|---|---|---|---|
| 8 | SAGE | • To determine the response of phytoplankton dynamics to iron addition in high nutrient low chlorophyll and low silicate (HNLCLSi) regions<br>• To test the assumption that the response of phytoplankton blooms to artificial iron addition can be detected by the enhanced air-sea exchanges of climate-relevant gases | • No shift to a diatom-dominated community<br>• No detection of fertilization-induced export | • High dilution rate by small patch size |
| 9 | LOHAFEX | • To trace the fate of iron-stimulated phytoplankton blooms and deep carbon export in HNLCSi regions | • Observation of all the phases of the phytoplankton bloom from onset to termination<br>• No shift to a diatom-dominated community<br>• No detection of fertilization-induced export<br>• High grazing pressure and active bacterial respiration | |
| 10 | SEEDS-1 | • To investigate the relationship between phytoplankton biomass/community and dust deposition in the subarctic North Pacific (NP)<br>• To investigate changes in phytoplankton composition and vertical carbon flux | • A shift from oceanic diatoms to fast-growing neritic ones<br>• The largest changes in biogeochemical parameters of all aOIF experiments<br>• No detection of large POC export flux | • Single iron addition<br>• Insufficient experimental duration |
| 11 | SERIES | • To compare the response of phytoplankton in eastern subarctic with that in the western subarctic ecosystem<br>• To investigate the most significant factor that controls the beginning to the ending of the phytoplankton bloom induced by iron addition | • Observation of all phases of the phytoplankton bloom from onset to termination<br>• No significant increases in export fluxes below the mixed layer depth<br>• High bacterial remineralization and mesozooplankton grazing pressure | |
| 12 | SEEDS-2 | • To investigate the most significant factor that controls the beginning to the ending of the phytoplankton bloom induced by iron addition | • Observation of all phases of the phytoplankton bloom from onset to termination<br>• No shift to a diatom-dominated community<br>• No significant increases in export fluxes<br>• Extensive copepod grazing | |
| 13 | FeeP | • To investigate the impact of iron and phosphate co-limitation on PP | • Increases in pico-phytoplankton abundances | |

Sources are Martin et al. (1994); Coale et al. (1996); Coale et al. (1998); Bidigare et al. (1999); Boyd et al. (2000); Charette and Buesseler (2000); Gervais et al. (2002); Tsuda et al. (2003); Boyd et al. (2004); Coale et al. (2004); Bakker et al. (2005); Boyd et al. (2005); de Baar et al. (2005); Hiscock and Millero (2005); Nishioka et al. (2005); Tsuda et al. (2005); Tsumune et al. (2005); Boyd et al. (2007); Rees et al. (2007); Tsuda et al. (2007); Harvey et al. (2010); Law et al. (2011); Smetacek et al. (2012); and Martin et al. (2013).

**Table 3.** Initial conditions and changes (Δ values) in chemical parameters during the artificial ocean iron fertilization (aOIF) experiments

| | Experiment | Initial $NO_3^-$ (µM) | $\Delta NO_3^-$ (µM) | Initial $PO_4$ (µM) | $\Delta PO_4$ (µM) | Initial Si (µM) | ΔSi (µM) | Initial $pCO_2$ (µatm) | $\Delta pCO_2$ (µatm) | Initial DIC (µM) | ΔDIC (µM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | 10.8 | -0.70 | 0.92 | -0.02 | 3.90 | -0.02 | 471 | -13.0 | 2044 | [**]-6.00 |
| 2 | IronEx-2 | 10.4 | -4.00 | 0.80 | -0.25 | 5.10 | -4.00 | 538 | -73.0 | 2051 | [**]-27.0 |
| 3 | SOIREE | 25.0 | -2.90 | 1.50 | -0.24 | 10.0 | -2.90 | 349 | -(38.0–32.0) | | -(18.0–15.0) |
| 4 | EisenEx | 22.0 | -1.00 | 1.60 | -0.10 | 10.0 | 0 | ~360 | -(20.0–18.0) | | -(15.0–12.0) |
| 5 | SOFeX-N | 21.9 | -1.40 | 1.40 | -0.09 | 2.50 | -1.10 | 367 | -26.0 | 2109 | -14.0 |
| 6 | SOFeX-S | 26.3 | -3.50 | 1.87 | -0.21 | 62.8 | -4.00 | 365 | -36.0 | 2176 | -21.0 |
| 7 | EIFEX | 25.0 | -1.60 | 1.80 | [†]~-0.30 | 19.0 | -11.0 | 360 | -30.0 | 2135 | -13.5 |
| 8 | SAGE | 7.90–10.5 | 1.30–3.90 | 0.62–0.85 | | 0.83–0.97 | | 330 | 8.00 | 2057 | 25.0 |
| 9 | LOHAFEX | 20.0 | -2.50 | 1.20–1.30 | [‡]~-0.15 | 0.60–1.60 | | [*]~358 | -(15.0–7.00) | | |
| 10 | SEEDS-1 | 18.5 | -15.8 | | | 31.8 | -26.8 | 390 | -130 | | -58.0 |
| 11 | SERIES | 10.0–12.0 | -(8.50–6.50) | 1.00 | -0.50 | 14.0–16.0 | -(13.6–11.6) | 350 | -85.0 | 2030 | -37.0 |
| 12 | SEEDS-2 | 18.4 | -5.70 | | | 36.1 | | 370 | -6.00 | | |
| 13 | FeeP | <0.01 | | ~0.01 | | | | | | | ~-1.00 |

[†]$\Delta PO_4$ in EIFEX was digitized from Figure 3 of Smetacek et al. (2012); [‡]$\Delta PO_4$ in LOHAFEX was digitized from Figure 5.1 of Smetacek and Naqvi (2010). [*]$\Delta pCO_2$ in LOHAFEX was digitized from Figure 6.1 of Smetacek and Naqvi (2010). [**]Dissolved inorganic carbon (DIC) values in IronEx-1/-2 indicate normalized DIC (normalized DIC = DIC × 35/Salinity).

Sources are Martin et al. (1994); Steinberg et al. (1998); Boyd et al. (2000); Bakker et al. (2001); Frew et al. (2001); Gervais et al. (2002); Bakker et al. (2005); Boyd et al. (2005); Hiscock and Millero (2005); Smetacek et al. (2005); Takeda and Tsuda (2005); Tsuda et al. (2005); Marchetti et al. (2006); Wong et al. (2006); Boyd et al. (2007); Tsuda et al. (2007); Tsumune et al. (2009); Harvey et al. (2010); Smetacek and Naqvi (2010); Berg et al. (2011); Currie et al. (2011); Law et al. (2011); Smetacek et al. (2012); Assmy et al. (2013); Ebersbach et al. (2014); and Latasa et al. (2014).

**Table 4.** Initial values of biological parameters and the values after fertilization. Note that maximum values were attained after fertilization.

| - | Experiment | Initial Fv/Fm | After Fv/Fm | Initial Chlorophyll-a (mg m$^{-3}$) | After Chlorophyll-a (mg m$^{-3}$) | Initial PP (mg C m$^{-2}$ d$^{-1}$) | After PP (mg C m$^{-2}$ d$^{-1}$) | Initial Mesozooplankton biomass (mg C m$^{-3}$) | After Mesozooplankton biomass (mg C m$^{-3}$) | Initial Heterotrophic Bacteria abundance (× 10$^5$ cells ml$^{-1}$) | After Heterotrophic Bacteria abundance (× 10$^5$ cells ml$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | ~0.30 | 0.63 | 0.24 | 0.65 | [*]300–450 | [*]805–1330 | | | | |
| 2 | IronEx-2 | 0.25 | [¶]~0.57 | 0.15–0.20 | 4.00 | [**]~630 | [**]~2430 | 3.8 (0–55 m) | 6.6 (0–55 m) | 9.5 | |
| 3 | SOIREE | 0.22 | 0.65 | 0.25 | 2.00 | [***]~120 | [***]~1300 | [†]22.8 (0–65 m) | [†]30.1 (0–65 m) | 3.7 | |
| 4 | EisenEx | 0.30 | 0.56 | 0.50 | 2.50 | 130–220 | 790 | | | 4.0 | |
| 5 | SOFeX-N | 0.20 | 0.5 | [‡]~0.15 | [‡]~2.60 | [§]~144 | [§]~1500 | | | 4.0 | |
| 6 | SOFeX-S | 0.25 | 0.65 | [‡]~0.30 | [‡]~3.80 | [§]~216 | [§]~972 | | | 4.0 | |
| 7 | EIFEX | [¶¶]~0.28 | [¶¶]~0.6 | 0.70 | 3.16 | ~750 | 1500 | | | | |
| 8 | SAGE | 0.27 | 0.61 | 0.63 | 1.33 | 540 | 900 | | | | |
| 9 | LOHAFEX | ~0.33 | 0.50 | 0.50 | 1.25 | <960 | 1560 | | | | |
| 10 | SEEDS-1 | [¶¶¶]~0.19 | [¶¶¶]~0.42 | 0.80–0.90 | 21.8 | 420 | 1670 | [†]6.8 (0–20 m) | [†]7.5 (0–20 m) | 2.5 | |
| 11 | SERIES | 0.24 | 0.55 | 0.35 | ~5.00 | 300 | >2000 | [†]7.3 (0–30 m) | | 5.5 | 12 |
| 12 | SEEDS-2 | 0.29 | [¶¶¶¶]~0.43 | 0.80 | 2.48 | 390 | >1000 | [†]18.9 (0–20 m) | [†]38 (0–20 m) | | |
| 13 | FeeP | - | - | 0.06 | 0.07 | - | - | | | | |

[¶]Fv/Fm in IronEx-2 was digitized from the Figure 3 of Behrenfeld et al. (1996); [¶¶]Fv/Fm in EIFEX was digitized from the Figure 2 of Berg et al. (2011); [¶¶¶]Fv/Fm in SEEDS-1 was digitized from the Figure 2 of Tsuda et al. (2003); [¶¶¶¶]Fv/Fm in SEEDS-2 was digitized from the Figure 6 of Tsuda et al. (2007). [‡]Chlorophyll-a concentrations in SOFeX-N/S were digitized from the supplementary Figure 5 of Coale et al. (2004). [*]Primary productivity (PP) in IronEx-1 was estimated by multiplying PP (mg C m$^{-3}$ d$^{-1}$) with the mixed layer depth (initial: 30 m and after: 35 m); [**]PP in IronEx-2 was digitized from the Figure 2 of Boyd (2002); [***]PP in SOIREE was digitized from the Figure 3 of Gall et al. (2001a); [§]PP values in SOFeX-N/S were digitized from the Figure 4 of Coale et al. (2004). [†]Mesozooplankton biomass indicates copepod biomass; Values in brackets correspond to the sampling layer; After mesozooplankton biomass is the mean value averaged for the experimental period after iron addition.

Sources are Kolber et al. (1994); Behrenfeld et al. (1996); Coale et al. (1996); Steinberg et al. (1998); Boyd et al. (2000); Rollwagen and Landry (2000); Boyd and Law (2001); Gall et al., (2001a); Zeldis et al. (2001); Boyd (2002); Gervais et al. (2002); Tsuda et al. (2003); Boyd et al. (2004); Coale et al. (2004); Boyd et al. (2005); de Baar et al. (2005); Takeda and Tsuda (2005); Tsuda et al. (2005); Levasseur et al. (2006); Boyd et al. (2007); Tsuda et al. (2007); Kudo et al. (2009); Tsuda et al. (2009); Harvey et al. (2010); Berg et al. (2011); Currie et al. (2011); Peloquin et al. (2011); Smetacek et al. (2012); Thiele et al. (2012); and Martin et al. (2013).

**Table 5**. Initial values of the export flux and the values after fertilization (mg C $m^{-2}$ $d^{-1}$), the corresponding depth inside and outside the fertilized patch for artificial ocean iron fertilization (aOIF) experiments, and measurement method. Values in brackets correspond to the day of measurement after fertilization.

| | Experiment | In-patch Initial (day) | In-patch After (day) | Outside-patch Initial (day) | Outside-patch After (day) | Depth (m) | Method |
|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | | | | | | |
| 2 | IronEx-2 | 84 (0) | 600 (10) | | | 25 | Water-column $^{234}Th$ |
| 3 | SOIREE | | ~87 | | | 100 | Water-column $^{234}Th$ |
| | | | 185 (11–13) | 146 (0–2) | 78 (11–13) | 110 | Drifting trap |
| | | | 74 (11–13) | 73 (0–2) | 38 (11–13) | 310 | Drifting trap |
| 4 | EisenEx | | | | | | |
| 5 | SOFeX-N | | | | | | |
| 6 | SOFeX-S | 36 (5) | 112 (27) | 48 (6) | 49 (26) | 50 | Water-column $^{234}Th$ |
| | | 19 (5) | 142 (27) | 38 (6) | 56 (26) | 100 | Water-column $^{234}Th$ |
| 7 | EIFEX | *~340 (0) | *~1692 (32) | *~396 (0) | *~516 (32) | 100 | Water-column $^{234}Th$ |
| 8 | SAGE | | | | | | |
| 9 | LOHAFEX | **~60 (0) | **~94 (25) | **~78 (4) | **~97 (23) | 100 | Water-column $^{234}Th$ |
| 10 | SEEDS-1 | 234 (1–3) | 141 (12–14) | 148 (1–6) | 154 (10–14) | 40 | Drifting trap |
| | | 100 (0–2) | 423 (9–13) | | | 50 | †Water-column $^{234}Th$ |
| | | 68 (1–3) | 85 (12–14) | 61 (1–6) | 91 (10–14) | 100 | Drifting trap |
| | | 121 (0–2) | 460 (2–9) | | | 200 | Water-column $^{234}Th$ |
| 11 | SERIES | ‡~120 (3) | 480 (24) | 192 (3) | 139 (15) | 50 | Drifting trap |
| | | ‡~48 (3) | ‡~192 (24) | | | 100 | Drifting trap |
| 12 | SEEDS-2 | 290 (1–4) | 580 (19–22) | 300 (1–8) | 509 (18–31) | 40 | Drifting trap |
| | | 316 (1–4) | 337 (19–22) | 213 (1–8) | 204 (18–31) | 100 | Drifting trap |
| 13 | FeeP | | | | | | |

*Export flux in EIFEX was digitized from the supplementary Figure 5.1 of Smetacek et al. (2012); **Export flux in LOHAFEX was digitized from the Figure 4 of Martin et al. (2013); †Export flux in SEEDS-1 was determined from the suspended particles; ‡Export flux in SERIES was digitized from the Figure 2 of Boyd et al. (2004).

Sources are Bidigare et al. (1999); Charette and Buesseler (2000); Nodder and Waite (2001); Boyd et al. (2004); Aono et al. (2005); Buesseler et al. (2005); Aramaki et al. (2009); Smetacek et al. (2012); and Martin et al. (2013).

## Figure Captions

**Fig. 1.** Diagram showing the monthly atmospheric $CO_2$ concentrations (ppm) (blue) measured at the Mauna Loa Observatory, Hawaii (http://www.esrl.noaa.gov/gmd/ccgg/trends/data.html), global monthly land surface air and sea surface temperature anomalies (°C) (red) (http://data.giss.nasa.gov/gistemp/), and pH (green) measured at ALOHA station in the central Pacific (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt). The data values represent moving average values for 12 months and shading indicates the standard deviation for 12 months.

**Fig. 2.** Schematic representation of several proposed climate-engineering methods (modified from Matthews (1996)).

**Fig. 3.** The iron hypothesis, as suggested by Martin (1990). (a) Effectiveness of the biological pump under normal conditions, (b) Effectiveness of the biological pump following iron enrichment (modified from Sarmiento and Gruber (2006)), and (c) Schematic diagram of the decrease in the downward flux of organic carbon as a function of depth in the water column (modified from Lampitt et al. (2008)). OM is organic matter.

**Fig. 4.** Global annual distribution of surface (a) Chlorophyll concentrations (mg $m^{-3}$), (b) Nitrate concentrations (μM), and (c) Silicate concentrations (μM). The chlorophyll-a concentration distribution was obtained from the Aqua MODIS chlorophyll-a composite from July 2002 to February 2016 (http://oceancolor.gsfc.nasa.gov/cgi/l3), nitrate and silicate were obtained from the World Ocean Atlas 2013 dataset (https://odv.awi.de/en/data/ocean/world_ocean_atlas_2013) and plotted using Ocean Data View (Schlitzer, 2017). The white circles indicate the locations of 13 artificial ocean iron fertilization (aOIF) experiments and the black triangles indicate the locations of two natural OIF (nOIF) experiments. Note that the numbers indicate the order of the aOIF experiments and the Roman-numerals indicate the order of the nOIF experiments (see Table 1).

**Fig. 5.** Photographs of the iron addition procedure. Panels a-f taken during the European Iron Fertilization Experiment (EIFEX), Surface Ocean Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange (SAGE), and Indo-German iron fertilization experiment (LOHAFEX): (a) Iron (II) sulfate bags. (b) The funnel used to pour iron and hydrochloric acid. (c) Tank system used for mixing Iron(II) sulfate, hydrochloric acid, and seawater (Smetacek, 2015). (d) Preparation for release: the deck of RV *Tangaroa* with the iron tanks on the left and the $SF_6$ tracer tanks on the right (Photo: Matt Walkington) (https://www.niwa.co.nz/coasts-and-oceans/research-projects/sage). (e) Outlet pipe connected to the tank system. (f) Pumping iron into the prop wash during EIFEX (Smetacek, 2015).

**Fig. 6.** (a) Maximum (bar with dotted line) and initial (bar with solid line) patch size ($km^2$) during artificial ocean iron fertilization (aOIF) experiments. (b) Total (bar with dotted line) and initial (bar with solid line) iron(Ⅱ) added (kg). (c) Maximum (bar with dotted line) and minimum (bar with solid line) mixed layer depth (MLD) (m) during aOIF experiments. (d) Initial sea surface temperature (SST, °C). (e) Initial nitrate concentrations (μM). (f) Initial silicate concentrations (μM). (g) Initial Fv/Fm ratios. (h) Initial chlorophyll-a concentrations (mg $m^{-3}$). Note that the numbers indicate the order of aOIF experiments as given in Fig. 4 and Table 1 and are grouped according to ocean basins; Equatorial Pacific (EP) (yellow bar), Southern Ocean (SO) (blue bar), subarctic North Pacific (NP) (red bar), and subtropical North Atlantic (NA) (green bar). Sources are Kolber et al. (1994); Martin et al. (1994); Behrenfeld et al. (1996); Coale et al. (1996); Coale et al. (1998); Steinberg et al. (1998); Boyd et al. (2000); Boyd and Law (2001); Gall et al. (2001b); Gervais et al. (2002); Law et al. (2003); Tsuda et al. (2003); Coale et al. (2004); Turner et al. (2004); Bakker et al. (2005); Boyd et al. (2005); de Baar et al. (2005); Hiscock and Millero (2005); Takeda and Tsuda (2005); Tsuda et al. (2005); Tsumune et al. (2005); Law et al. (2006); Marchetti et al. (2006); Boyd et al. (2007); Rees et al. (2007); Tsuda et al. (2007); Suzuki et al. (2009); Tsumune et al. (2009); Harvey et al. (2010); Smetacek and Naqvi (2010); Berg et al. (2011); Hadfield (2011); Law et al. (2011); Peloquin et al. (2011); Smetacek et al. (2012); Thiele et al. (2012); Martin et al. (2013); Ebersbach et al. (2014); and Latasa et al. (2014).

**Fig. 7.** (a) Maximum (bar with dotted line) and initial (bar with solid line) Fv/Fm ratios during artificial ocean iron fertilization (aOIF) experiments. (b) Changes in nitrate concentrations ($\Delta NO_3^- = [NO_3^-]_{post\text{-}fertilization\ (posf)} - [NO_3^-]_{pre\text{-}fertilization\ (pref)}$; μM). (c) Maximum (bar with dotted line) and initial (bar with solid line) chlorophyll-a concentrations (mg $m^{-3}$). (d) Distributions of chlorophyll-a concentrations (mg $m^{-3}$) on day 24 after iron addition in the Southern Ocean iron experiment-north (SOFeX-N) and on day 20 in the SOFeX-south (SOFeX-S) (white dotted box indicates phytoplankton bloom during OIF experiments). (e) Changes in primary productivity (PP) ($\Delta PP = [PP]_{postf} - [PP]_{pref}$; mg C $m^{-2}$ $d^{-1}$). (f) Changes in partial pressure of $CO_2$ ($pCO_2$) ($\Delta pCO_2 = [pCO_2]_{postf} - [pCO_2]_{pref}$; μatm). The color bar indicates changes in dissolved inorganic carbon (DIC) ($\Delta DIC = [DIC]_{postf} - [DIC]_{pref}$; μM). Note that the PP (mg C $m^{-2}$ $d^{-1}$) of aOIF experiment number 1 (IronEx-1) was estimated by multiplying the PP (mg C $m^{-3}$ $d^{-1}$) with the mixed layer depth (initial: 30 m and after: 35 m). The numbers on the X axis indicate the order of aOIF experiments as given in Fig. 4 and Table 1 and are grouped according to ocean basins; Equatorial Pacific (EP) (yellow bar), Southern Ocean (SO) (blue bar), subarctic North Pacific (NP) (red bar), and subtropical North Atlantic (NA)

(green bar). Sources are Kolber et al. (1994); Martin et al. (1994); Behrenfeld et al. (1996); Coale et al. (1996); Steinberg et al. (1998); Boyd et al. (2000); Boyd and Law (2001); Frew et al. (2001); Gall et al. (2001a); Boyd (2002); Gervais et al. (2002); Tsuda et al. (2003); Coale et al. (2004); Boyd et al. (2004); Bakker et al. (2005); Boyd et al. (2005); de Baar et al. (2005); Hiscock and Millero (2005); Smetacek et al. (2005); Takeda and Tsuda (2005); Tsuda et al. (2005); Wong et al. (2006); Boyd et al. (2007); Tsuda et al. (2007); Kudo et al. (2009); Tsumune et al. (2009); Harvey et al. (2010); Smetacek and Naqvi (2010); Berg et al. (2011); Currie et al. (2011); Law et al. (2011); Peloquin et al. (2011); Smetacek et al. (2012); Thiele et al. (2012); Assmy et al. (2013); Martin et al. (2013); and Ebersbach et al. (2014).

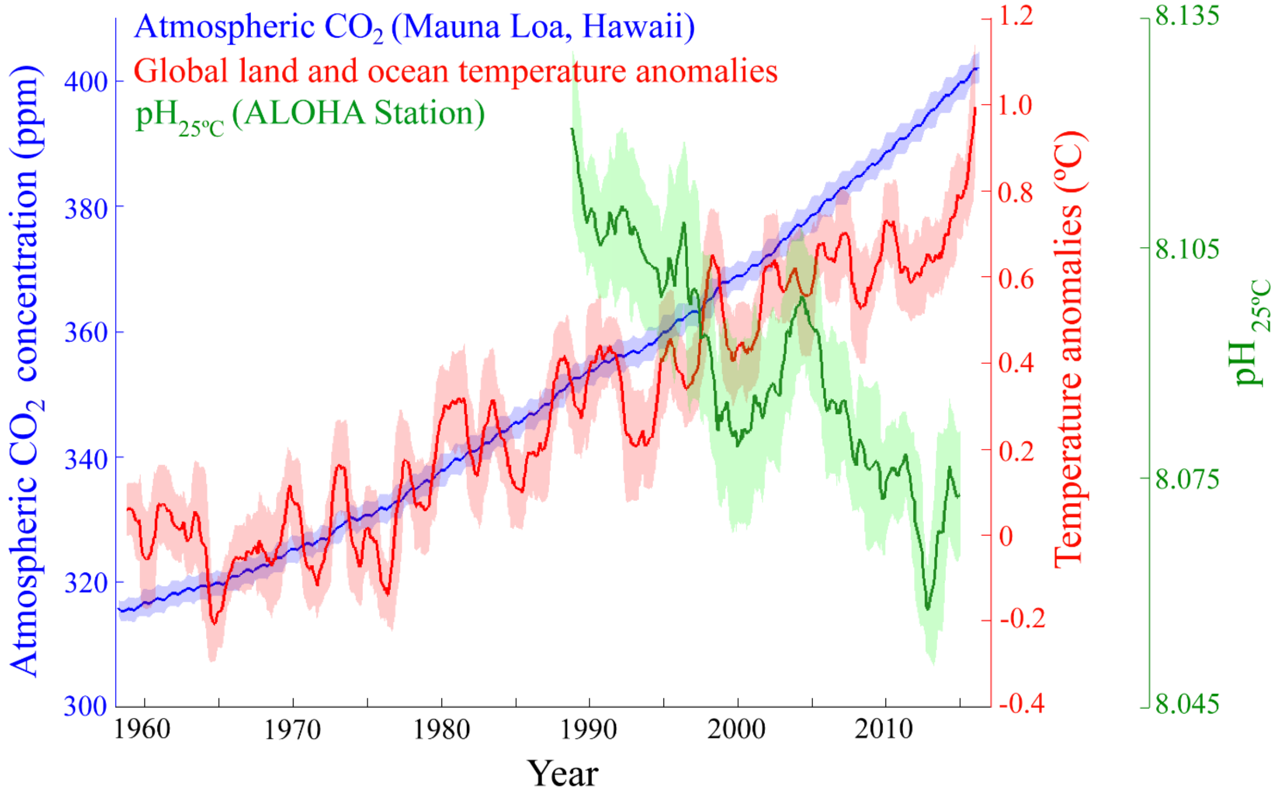
**Fig. 8.** (a) Time-series of particulate organic carbon (POC) fluxes estimated from the water-column based $^{234}$Th method (mg m$^{-2}$ d$^{-1}$) of the upper 100-m layer inside (red bar) and outside the fertilized patch (blue bar) during the European Iron Fertilization Experiment (EIFEX) (modified from Smetacek et al. (2012)). (b) Time-series of vertically integrated $^{234}$Th (dpm l$^{-1}$) inside (red circles) and outside the fertilized patch (blue diamonds) relative to the parent $^{238}$U (dpm l$^{-1}$; dotted black line) during the Southern Ocean Iron Release Experiment (SOIREE) (modified from Nodder et al. (2001)).

**Fig. 9.** Assessment framework for scientific research involving ocean fertilization (OF) (modified from Resolution LC-LP.2, 2010).

**Fig. 10.** (a) Time-series of mixed layer depth-integrated chlorophyll-a concentrations (mg m$^{-2}$) during the Southern Ocean Iron Release Experiment (SOIREE) (brown line), Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1 (SEEDS-1) (coral line), Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) (cyan line), SEEDS-2 (blue line), and European Iron Fertilization Experiment (EIFEX) (teal line). (b) The distributions of chlorophyll-a concentrations (mg m$^{-3}$) on day 5 and day 45 during SOIREE from SeaWiFS Level-2 daily images. Sources are Boyd and Abraham (2001); Tsuda et al. (2007); and Assmy et al. (2013).

**Fig. 11.** Schematic diagram of the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) representing the experiment target site (eddy structure) and survey methods (underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations).

**Fig. 1**



Atmospheric CO2 (Mauna Loa, Hawaii)
Global land and ocean temperature anomalies
pH25ºC (ALOHA Station)
Atmospheric CO2 concentration (ppm)
Temperature anomalies (ºC)
pH25ºC
Year
300
320
340
360
380
400
-0.4
-0.2
0
0.2
0.4
0.6
0.8
1.0
1.2
8.045
8.075
8.105
8.135
1960
1970
1980
1990
2000
2010

Fig. 2

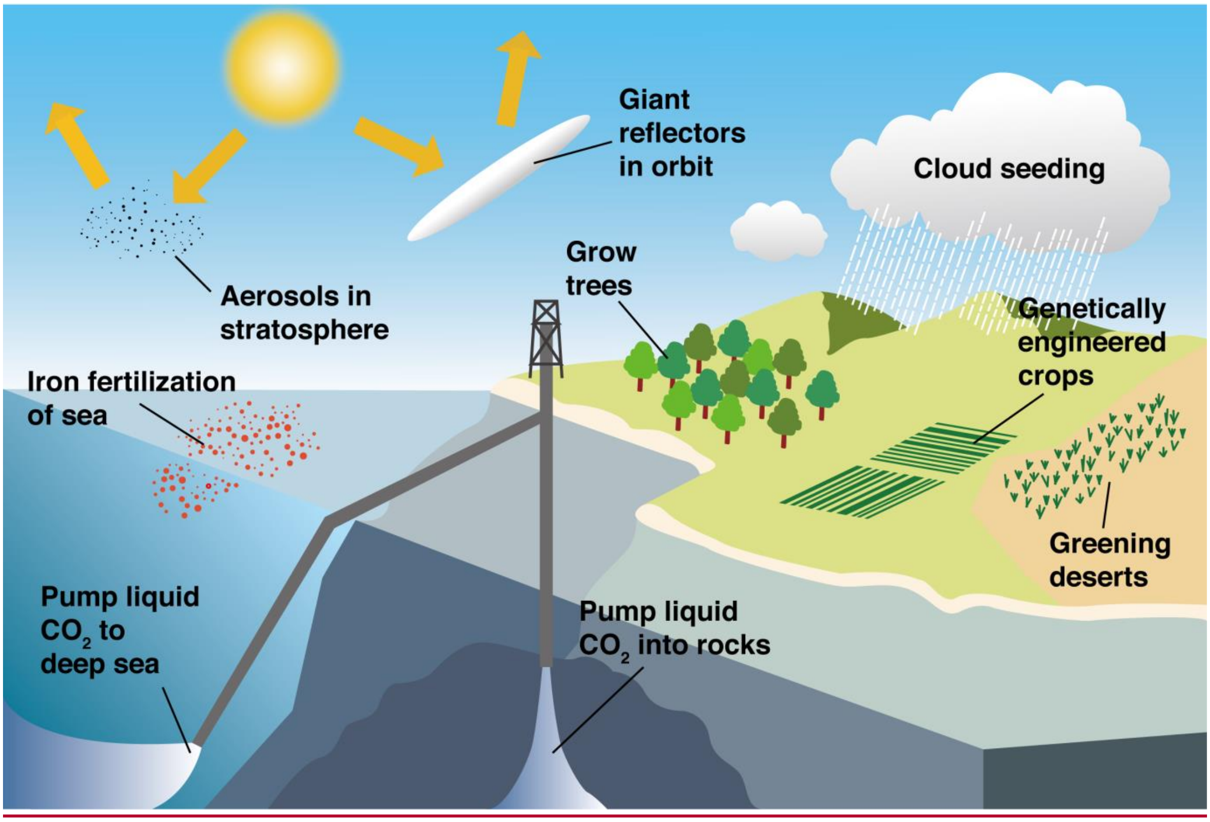

Giant
reflectors
in orbit
Cloud seeding
Aerosols in
stratosphere
Grow
trees
Genetically
engineered
crops
Iron fertilization
of sea
Greening
deserts
Pump liquid
$CO_2$ to
deep sea
Pump liquid
$CO_2$ into rocks

**Fig. 3**

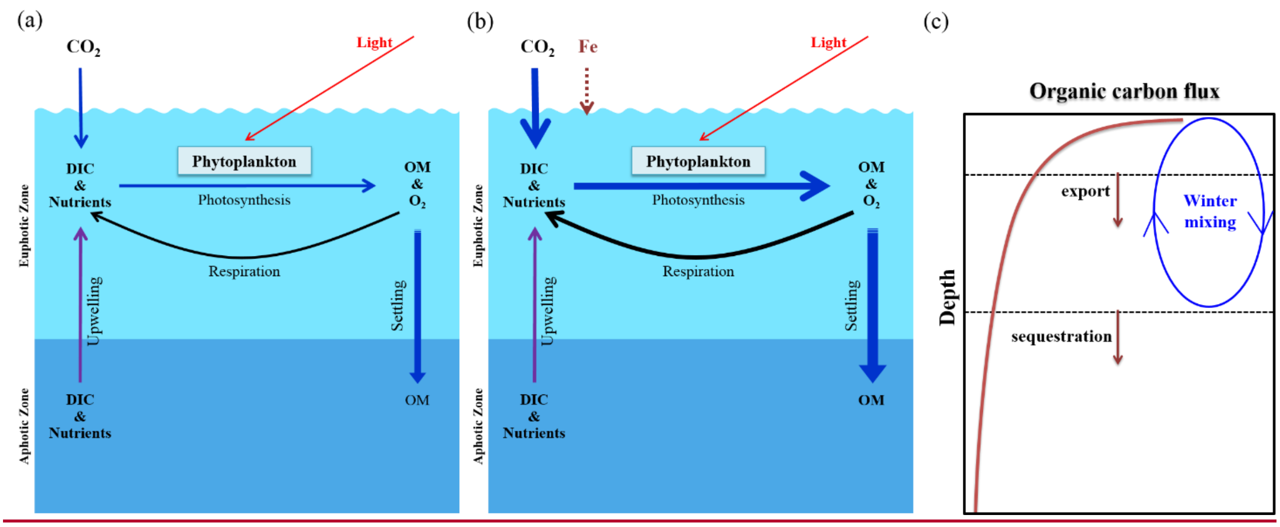
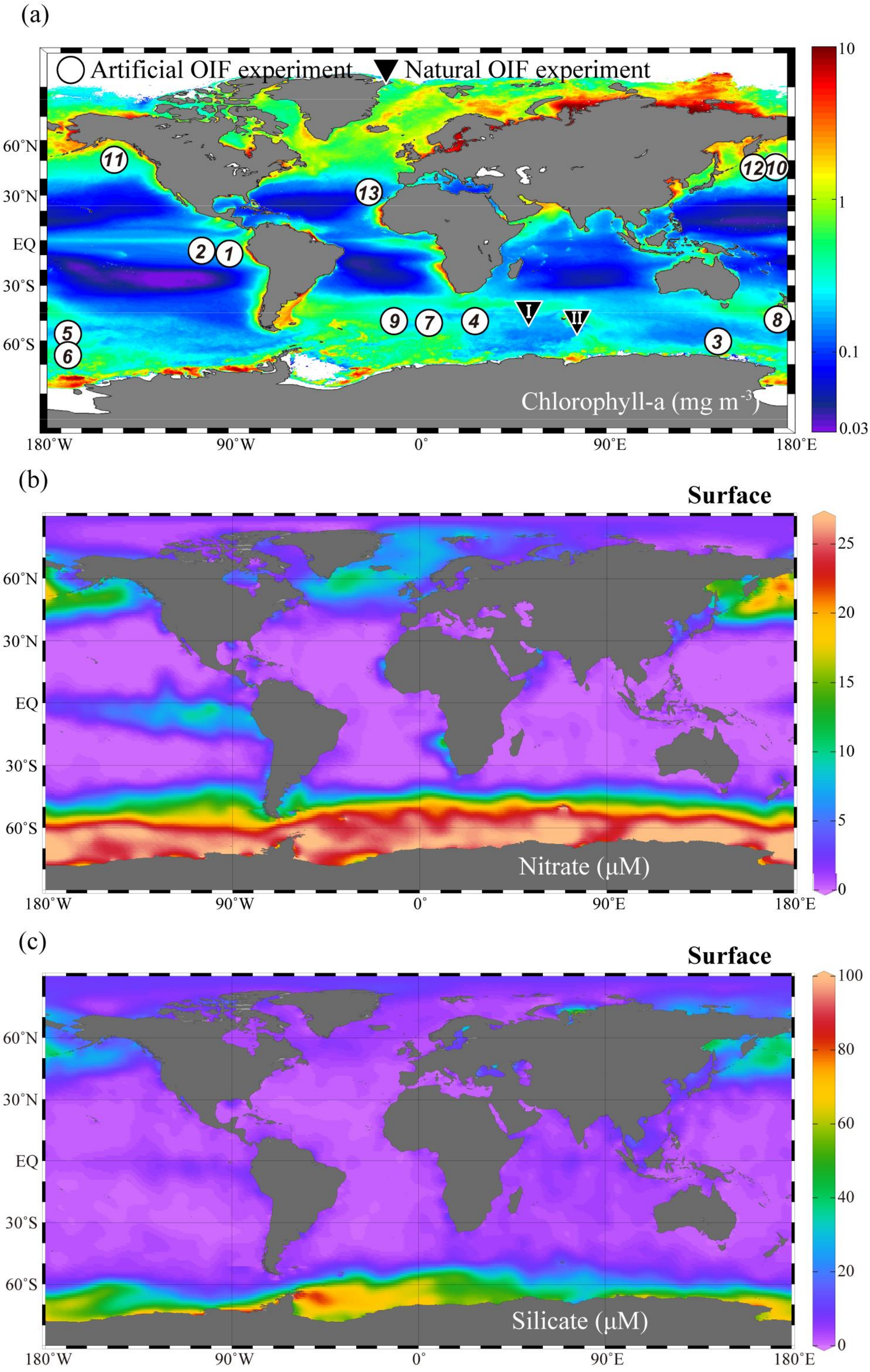

(a)
$CO_2$
Light
Phytoplankton
DIC & Nutrients
Photosynthesis
OM & $O_2$
Respiration
Euphotic Zone
Aphotic Zone
Upwelling
Settling
DIC & Nutrients
OM
(b)
$CO_2$
Fe
Light
Phytoplankton
DIC & Nutrients
Photosynthesis
OM & $O_2$
Respiration
Euphotic Zone
Aphotic Zone
Upwelling
Settling
DIC & Nutrients
OM
(c)
Organic carbon flux
Depth
export
Winter mixing
sequestration

**Fig. 4**



(a)
Artificial OIF experiment
Natural OIF experiment
Chlorophyll-a (mg m$^{-3}$)
60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
180°E
10
1
0.1
0.03
1
2
3
4
5
6
7
8
9
10
11
12
13
I
II
(b)
Surface
Nitrate (μM)
25
20
15
10
5
0
(c)
Surface
Silicate (μM)
100
80
60
40
20
0


(a)
(b)
(c)
(d)
(e)
(f)

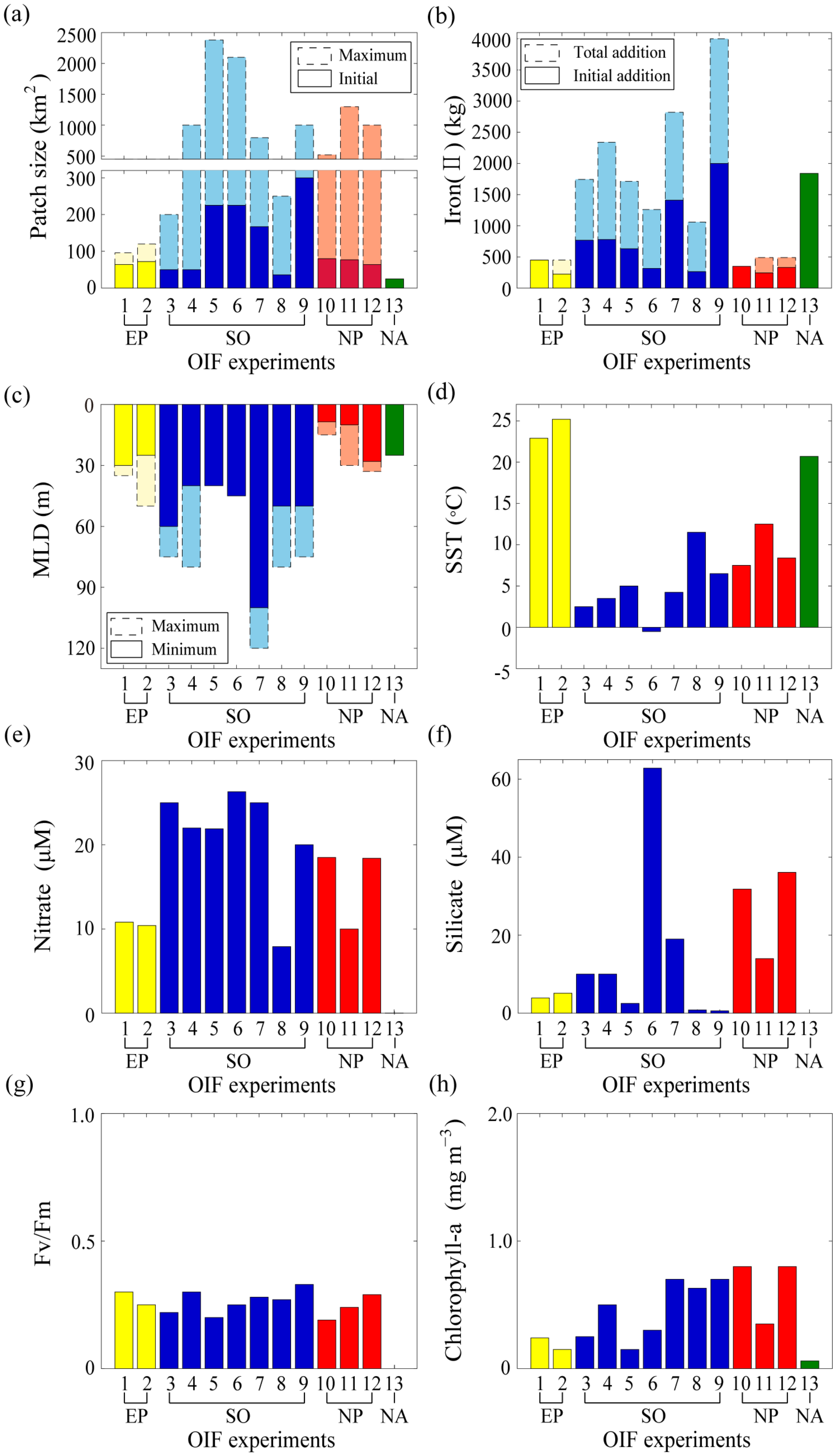

(a)
Patch size (km$^2$)
Maximum
Initial
(b)
Iron(II) (kg)
Total addition
Initial addition
(c)
MLD (m)
Maximum
Minimum
(d)
SST (°C)
(e)
Nitrate (μM)
(f)
Silicate (μM)
(g)
Fv/Fm
(h)
Chlorophyll-a (mg m$^{-3}$)
1 2 3 4 5 6 7 8 9 10 11 12 13
EP SO NP NA
OIF experiments

**Fig. 7**

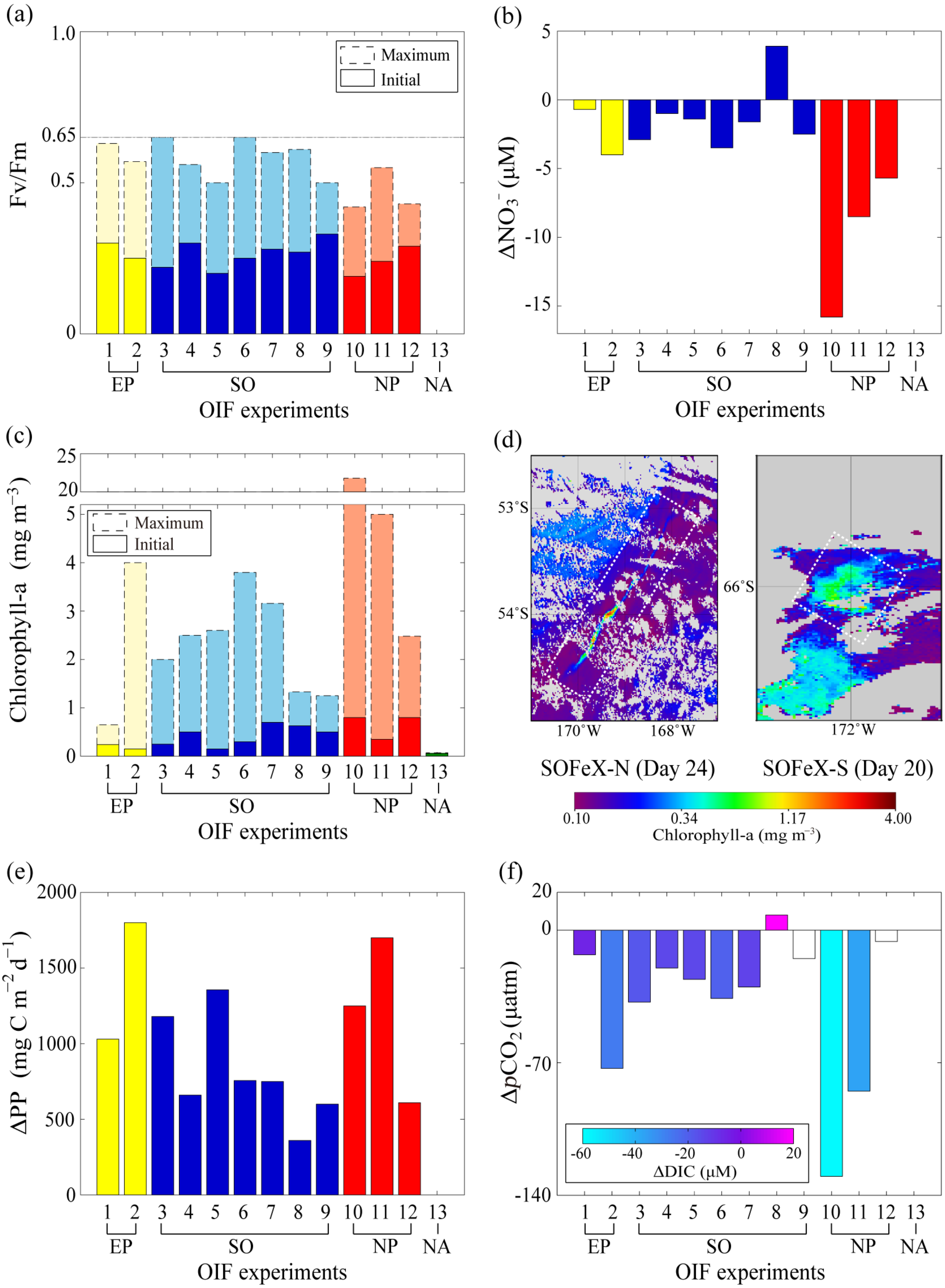

(a)
Fv/Fm
Maximum
Initial
OIF experiments
EP
SO
NP
NA
(b)
ΔNO3- (μM)
(c)
Chlorophyll-a (mg m-3)
(d)
53°S
54°S
66°S
170°W
168°W
172°W
SOFeX-N (Day 24)
SOFeX-S (Day 20)
Chlorophyll-a (mg m-3)
(e)
ΔPP (mg C m-2 d-1)
(f)
ΔpCO2 (μatm)
ΔDIC (μM)

**Fig. 8**

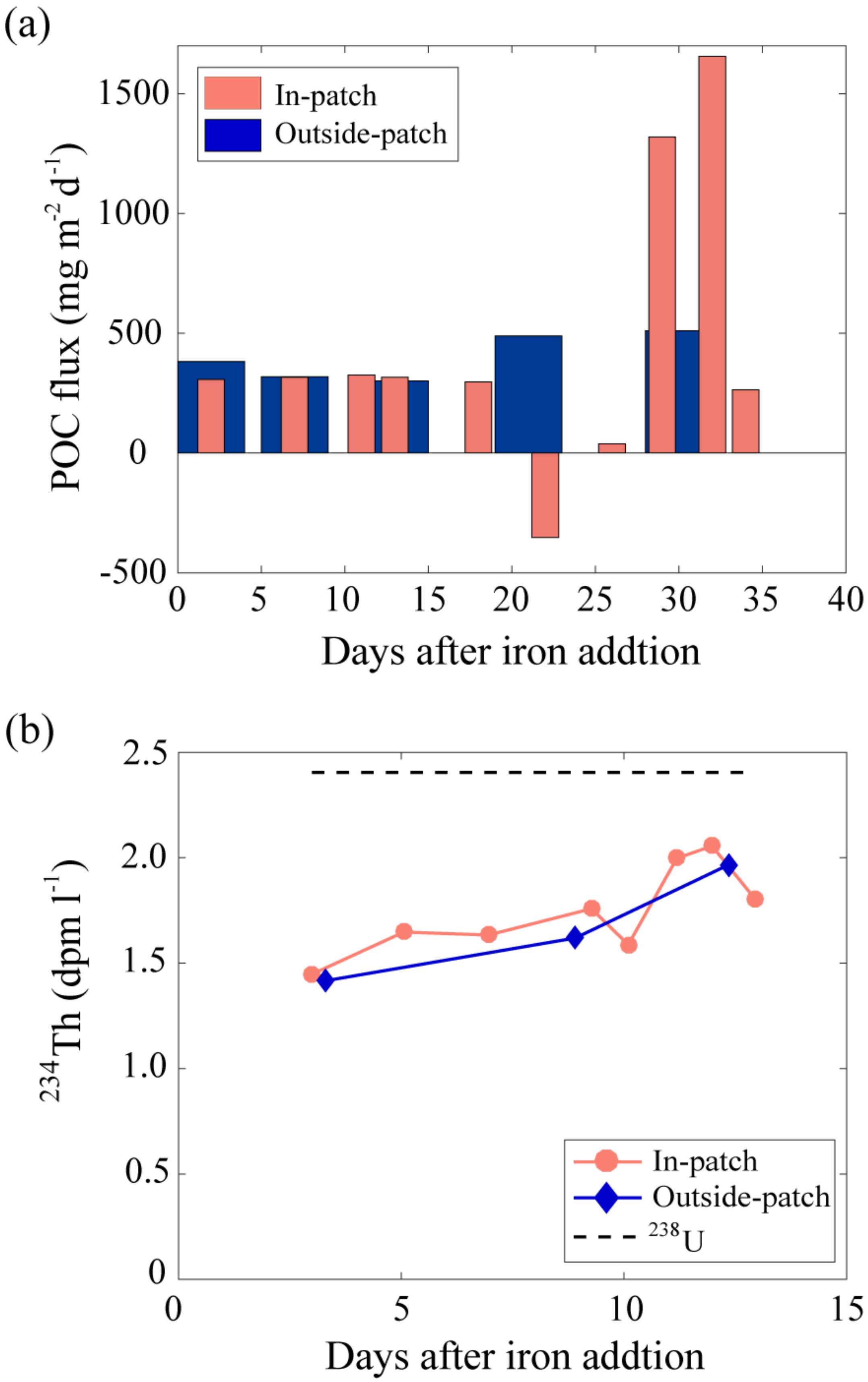

(a)
In-patch
Outside-patch
POC flux (mg m-2 d-1)
1500
1000
500
0
-500
0
5
10
15
20
25
30
35
40
Days after iron addtion
(b)
234Th (dpm l-1)
2.5
2.0
1.5
1.0
0.5
0
In-patch
Outside-patch
238U
0
5
10
15
Days after iron addtion

Fig. 9

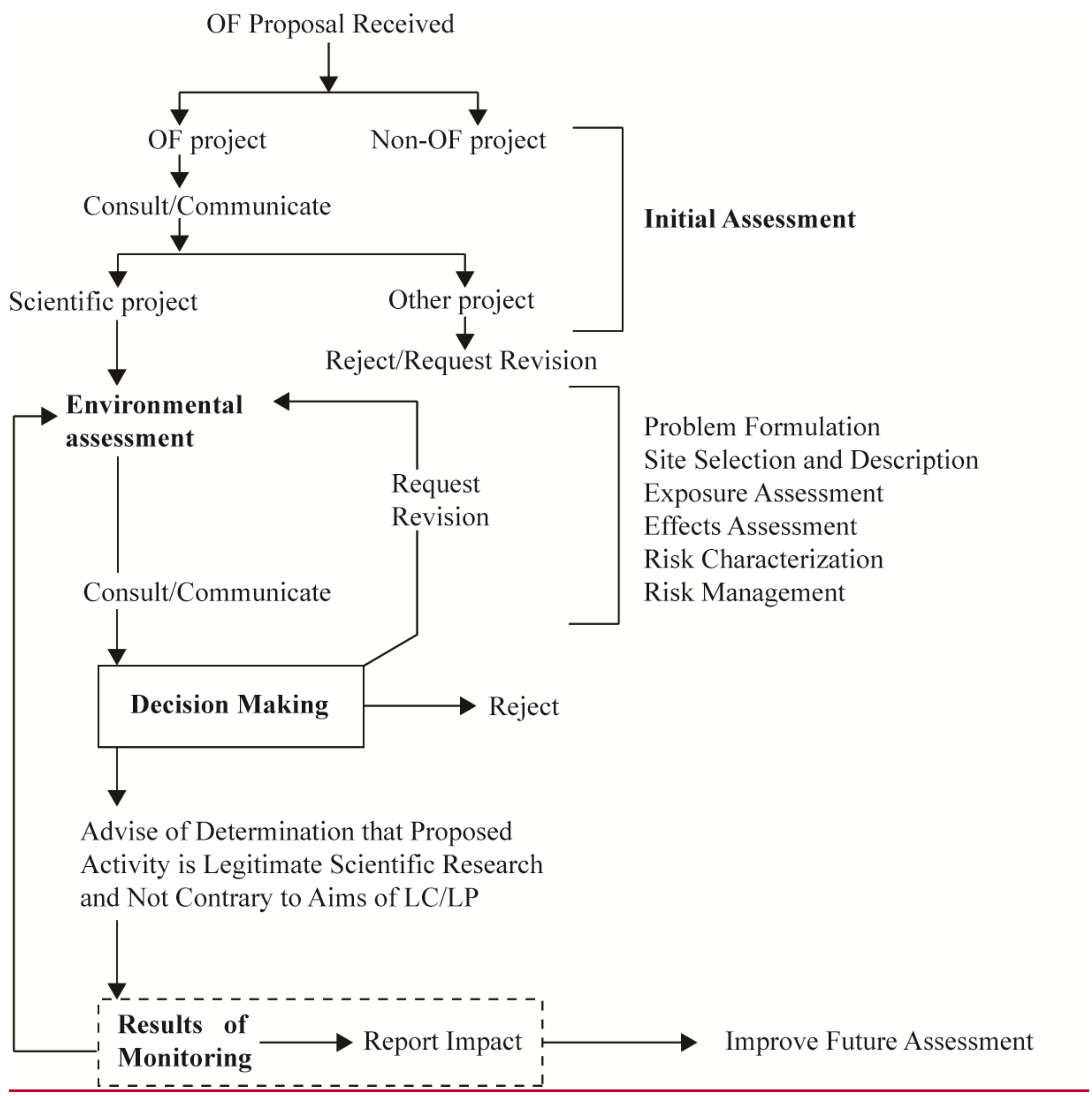

OF Proposal Received
OF project
Non-OF project
Consult/Communicate
Scientific project
Other project
Reject/Request Revision
Initial Assessment
Environmental assessment
Request Revision
Problem Formulation
Site Selection and Description
Exposure Assessment
Effects Assessment
Risk Characterization
Risk Management
Consult/Communicate
Decision Making
Reject
Advise of Determination that Proposed Activity is Legitimate Scientific Research and Not Contrary to Aims of LC/LP
Results of Monitoring
Report Impact
Improve Future Assessment

**Fig. 10**

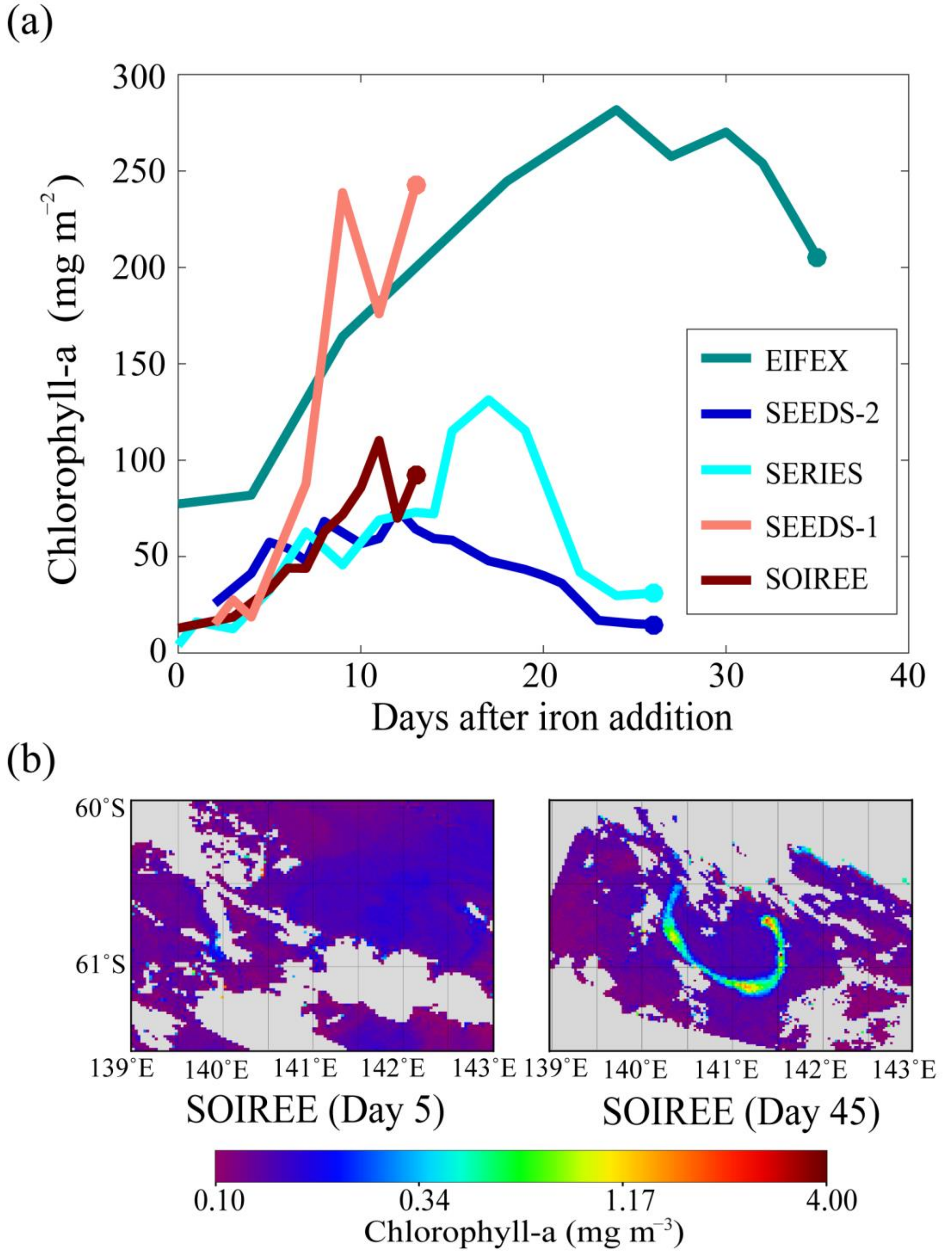
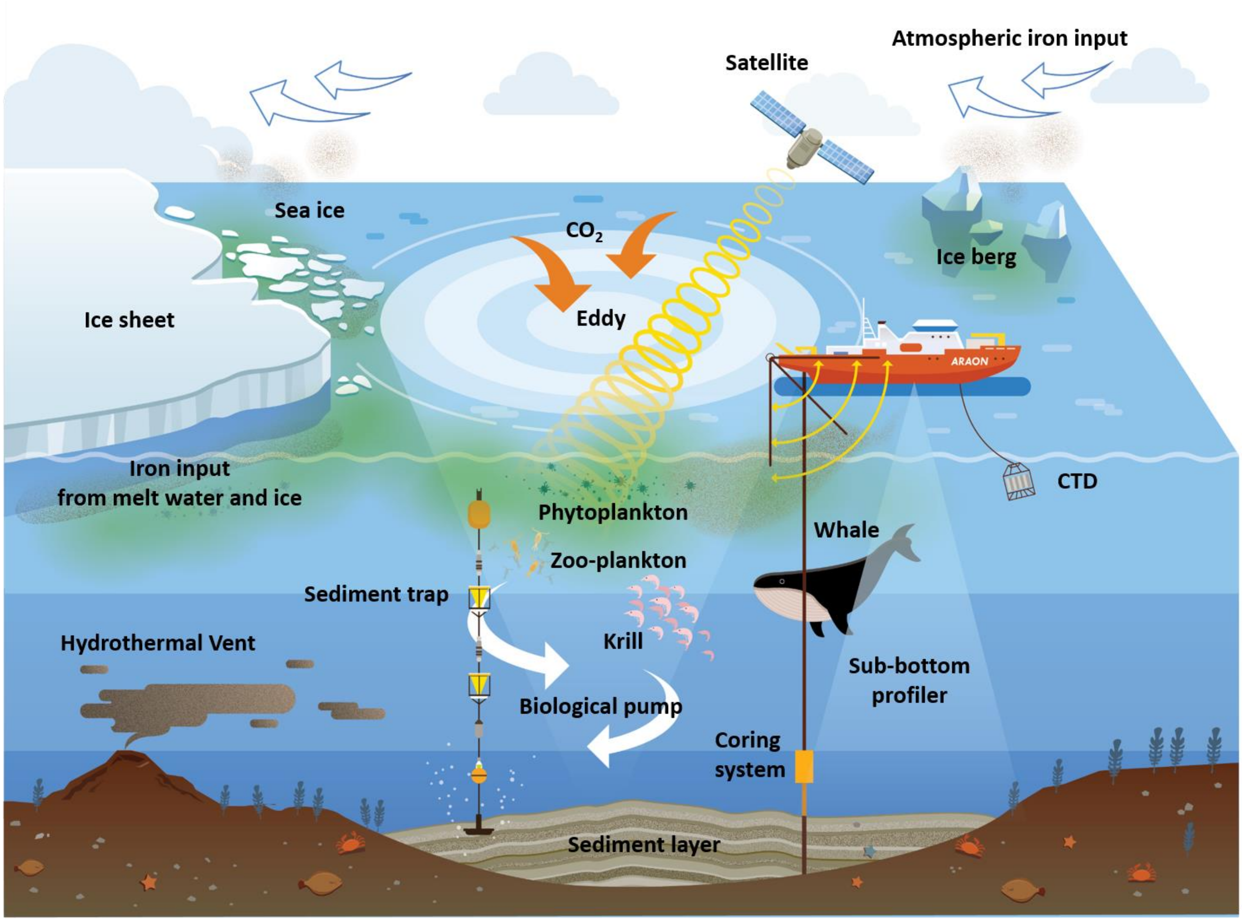

(a)
300
250
200
150
100
50
0
Chlorophyll-a (mg m$^{-2}$)
0
10
20
30
40
Days after iron addition
EIFEX
SEEDS-2
SERIES
SEEDS-1
SOIREE
(b)
60°S
61°S
139°E
140°E
141°E
142°E
143°E
SOIREE (Day 5)
SOIREE (Day 45)
0.10
0.34
1.17
4.00
Chlorophyll-a (mg m$^{-3}$)

Fig. 11



Atmospheric iron input
Satellite
Sea ice
$CO_2$
Ice berg
Ice sheet
Eddy
Iron input
from melt water and ice
ARAON
CTD
Phytoplankton
Whale
Zoo-plankton
Sediment trap
Krill
Hydrothermal Vent
Sub-bottom
profiler
Biological pump
Coring
system
Sediment layer

**Abstract.** Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric $CO_2$ concentrations, which have in turn been cited as the cause of a variety climate changes such as global warming and ocean acidification. Various approaches have been proposed to reduce atmospheric $CO_2$ concentrations. The 'Martin (or Iron) Hypothesis' suggests that ocean iron fertilization (OIF) should be an efficient method for stimulating the biological pump in iron-limited high nutrient low chlorophyll regions. To test the Martin hypothesis, a total 13 OIF experiments have been performed since 1990 in the Southern Ocean (7 times), in the subarctic Pacific (3 times), in the equatorial Pacific (twice), and in the subtropical Atlantic (once). These OIF field experiments demonstrated that primary production could be significantly increased after artificial iron addition. However, effectiveness in export production revealed by the OIF experiments was unexpectedly low compared to production from natural processes in all, except one of the experiments (i.e., the Southern Ocean European Iron Fertilization Experiment, EIFEX). These results, including possible side effects such as $N_2O$ production and hypoxia development, have been scientifically debated amongst those who support and oppose OIF experimentation. In the context of increasing global and political concerns associated with climate change, it is valuable to examine the validity and usefulness of the OIF. We provide a general overview of the OIF experiments conducted over the last 25 years (past), a discussion of OIF debates including possible side effects and international law (present), a suggestion of considerations for designing future OIF experiments to maximize the effectiveness of OIF (future), and an introduction to the OIF experiment design guidelines for a future Korean Iron Fertilization Experiment in the Southern Ocean.

**Keywords:** Ocean Iron Fertilization; High-Nutrient and Low-Chlorophyll regions; Biological Pump; Phytoplankton; Iron

## 1 Introduction

Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric $CO_2$ from ~280 ppm (pre-industry) to ~400 ppm (present) (http://www.esrl.noaa.gov/), which has in turn led a variety of climate changes such as global warming and ocean acidification (IPCC, 2013) (Fig. 1). As the Anthropocene climate system has rapidly changed toward the more unpredictable, scientific consensus is that the negative outcomes are a globally urgent issue that should be resolved in a timely manner for the sake of all lives on Earth (IPCC, 1990, 1992, 1995, 2001, 2007, 2013). Various ideas/approaches have been proposed to relieve/resolve the problem of global warming (Matthews, 1996; Lenton and Vaughan, 2009; Vaughan and Lenton, 2011; IPCC, 2014; Leung et al., 2014; Ming et al., 2014), largely based on two categories: (1) reduction of atmospheric $CO_2$ – ocean fertilization to enhance biological $CO_2$ uptake and/or direct capture or storage of atmospheric $CO_2$ through chemically engineered processes, and (2) control of solar radiation – artificial aerosol injection into the atmosphere to augment cloud formation and cloud brightening to elevate albedo (Fig. 2). One of the most attractive methods among the proposed approaches is *ocean fertilization* which targets the drawdown of atmospheric $CO_2$ by nutrient addition (e.g., iron, nitrogen or phosphorus compounds) to stimulate the phytoplankton growth via the ocean biological pump (ACE CRC, 2015).

The ocean biological pump (*a.k.a.* 'export production') is frequently depicted as a process whereby organic matter produced by phytoplankton during photosynthesis in surface waters is quickly transported to intermediate and/or deep waters (Fig. 3a) (Volk and Hoffert, 1985; De La Rocha, 2007). Although efficiency of the biological pump is mainly controlled by the supply of macro-nutrients (i.e., nitrate, phosphate, and silicate) into the euphotic zone leading to new production (Sarmiento and Gruber, 2006), iron acts as an essential micro-nutrient to stimulate the uptake of macro-nutrients for phytoplankton growth (Fig. 3b) (Martin and Fitzwater, 1988; Martin, 1990; Morel and Price, 2003). In the subarctic Pacific, equatorial Pacific, and Southern Ocean, which are well known as high-nutrient and low-chlorophyll (HNLC) regions (Fig. 4a and b), phytoplankton cannot completely utilize the available macro-nutrients (particularly nitrate) during photosynthesis due to a lack of iron. For this reason, primary production in these HNLC regions is relatively low in spite of the availability of nutrients (Fig. 4a and b).

It is thought, based on Arctic/Antarctic ice core analyses, that atmospheric $CO_2$ (~180 ppm) during the Last Glacial Maximum (LGM; ~20,000 years ago) was much lower than during pre-industrial times (~280 ppm) (Neftel et al., 1982; Barnola et al., 1987; Petit et al., 1999). Over the last 25 years, several hypotheses have been proposed to explain the mechanisms that lowered atmospheric $CO_2$ level during the LGM (Broecker, 1982; McElroy, 1983; Falkowski, 1997; Broecker and Henderson, 1998; Sigman and Boyle, 2000). One is particularly relevant to modern nutrient cycling in the Southern Ocean. In 1990, Martin hypothesized an LGM mechanism whereby the biological pump was substantially enhanced due to the relief of iron-limitation in HNLC regions, in particular the Southern Ocean, via high dust inputs (Fig. 3b). These dust inputs are generally regarded as one of major natural iron sources fertilizing oceans. He concluded with the now famous and often cited words "*Give me half a tanker of iron, and I will give you the next ice age*" (Martin, 1990). Since Martin's hypothesis was first published, there has been enormous interest in ocean iron fertilization (OIF) because only a small amount of iron (C:Fe ratios = 100,000:1, Anderson and Morel, 1982) is needed to stimulate a strong phytoplankton response. Therefore, much of the investigative focus has been centered on artificially adding iron to HNLC regions as a means of accelerating the ocean biological pump (ACE CRC, 2008).

To test the Martin's hypothesis, 2 natural and 13 artificial OIF experiments for scientific study have been performed to date in the subtropical Atlantic, equatorial Pacific, subarctic Pacific, and Southern Ocean (Blain et al., 2007; Pollard et al., 2009;

Strong et al., 2009) (Fig. 4a and Table 1). These OIF experiments demonstrated that primary production could be significantly increased after iron addition (de Baar et al., 2005; Boyd et al., 2007). To evaluate whether OIF has potential as a geoengineering strategy for carbon sequestration, not only the amount of carbon fixed by phytoplankton at the ocean surface but also the amount of carbon sequestered to the deep ocean must be considered in determining the effectiveness of OIF (Buesseler and Boyd, 2003). High export production/carbon sequestration effectiveness were observed from natural OIF experiments in the Southern Ocean near the Kerguelen Plateau and Crozet Islands (Blain et al., 2007; Pollard et al., 2009). However, the artificial OIF experiments showed unexpectedly weak responses compared to natural production in all the experiments (de Baar et al., 2005; Boyd et al., 2007), except one; the Southern Ocean European Iron Fertilization Experiment, EIFEX (Smetacek et al., 2012). These results, which include side effects such as $N_2O$ production and hypoxia development (Fuhrman and Capone, 1991), have been scientifically debated amongst those who support and oppose OIF experimentation (Chisholm et al., 2001; Johnson and Karl, 2002; Lawrence, 2002; Buesseler and Boyd, 2003; Williamson et al., 2012).

In the context of increasing global and political concerns associated with rapid climate change, it is still valuable to examine the validity and usefulness of artificial OIF experimentation as a climate change strategy. Therefore, the purpose of this paper is (1) to provide an overview of the OIF experiments conducted over the last 25 years, (2) to discuss the pros and cons of OIF, including possible side effects and international law, (3) to suggest considerations for designing future OIF experiments with maximum effectiveness, and (4) to introduce design guidelines for future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project.

## 2 Past: Overview of artificial OIF experiments

This overview of past OIF experimentation begins in Section 2.1 with a presentation of how each of the experiments was designed and why each was performed (Table 2). The unique prior ocean conditions for the various experiments are described in Section 2.2. Tracing the effects of iron addition is described in Section 2.3 and biogeochemical responses to the OIF experiments are presented in Section 2.4. Enhancement of carbon flux was assessed in Section 2.5 and why the outcomes of the experiments were so different and what has been learned from these experiments were discussed in Section 2.6 (Table 2).

### 2.1 Design/Objective of artificial OIF experiments

A total of 13 artificial OIF experiments have been conducted in the following areas: HNLC (i.e., nitrate >10 μM) regions such as the equatorial Pacific (twice), subarctic Pacific (3 times), and Southern Ocean (7 times), and one low-nutrient and low-chlorophyll (LNLC) (i.e., nitrate <10 μM) region, i.e., the subtropical Atlantic (once) (Table 1, Fig. 4a and b).

#### 2.1.1 OIF in the equatorial Pacific

The first OIF experiment, IronEx-1 (Table 1), was carried out over 10 days in October 1993 in the equatorial Pacific (Martin et al., 1994; Coale et al., 1998). This region, located to the south of the Galapagos Islands, was proposed as an optimal place to perform an OIF experiment because (1) the warm temperatures, high light intensity, and low cloud cover allowed for rapid phytoplankton growth, (2) the relatively large number of research cruises conducted in the region provided sufficient physical and biogeochemical property information, (3) it was easily accessible, and (4) it provided an opportunity to examine the natural relationship between primary production and iron addition (via iron inputs into open-ocean waters via the plumes off the western coast of Galapagos Islands) before artificial OIF experiment (Martin and Chisholm, 1992; Martin et al., 1994).

However, the magnitude of biogeochemical responses in IronEx-1 was not as dramatic as expected (Martin et al., 1994). Three hypotheses were advanced to explain the unexpectedly weak results: (1) the possibility of other unforeseen micro-nutrient (e.g., cadmium and manganese) limitations, (2) the short residence time of bioavailable iron in the experimental surface patch due to unstable water-column structure, and (3) the extremely high grazing stress placed on the patch by zooplankton (Cullen, 1995).

To investigate the unexpected responses revealed in IronEx-1, a second OIF experiment, IronEx-2, was conducted in May 1995 (Coale et al., 1996). The IronEx-2 research cruise occupied generally the same area for a longer period (17 days) providing more time to collect integrated information about the biogeochemical, physiological, and ecological responses to the OIF experiment. IronEx-2 demonstrated that massive phytoplankton blooming associated with OIF in the equatorial Pacific was possible, and it rekindled interest in and stimulated OIF experiments in other HNLC regions (Coale et al., 1996; Bidigare et al., 1999).

### 2.1.2 OIF in the Southern Ocean

The Southern Ocean, the largest HNLC region in the World Ocean, became the next region selected for OIF experimentation (Frost, 1996) because of its important role in intermediate and deep water formation, which suggested great potential for affecting the carbon sequestration associated with iron addition (Martin, 1990; Sarmiento and Orr, 1991; Cooper et al., 1996; Marshall and Speer, 2012). The Southern Ocean iron release experiment (SOIREE) (Table 1 and Fig. 4a), the first *in situ* OIF experiment performed in the Southern Ocean, took place in February 1999 (13 days) in the Australasian-Pacific sector of the Southern Ocean (Boyd et al., 2000). Iron-induced phytoplankton blooms confirmed that the supply of iron controls primary production in the Southern Ocean. It has also been shown that a model can produce LGM atmospheric $CO_2$ levels (~200 ppm) using SOIREE results with atmospheric dust flux obtained from the Vostok ice core analysis (Watson et al., 2000). The following year, a second Southern Ocean OIF experiment, EisenEx ('Eisen' is iron in German), was performed in November (23 days) in a closed cyclonic eddy of the Atlantic sector of the Southern Ocean (Smetacek, 2001).

The Southern Ocean exhibits markedly varied silicate concentrations on either side of the Antarctic Polar Front (PF): low silicate concentrations (<5 μM) to the north of the PF (<61° S) and high silicate concentrations (>60 μM) to the south of the PF (>61° S) (Fig. 4c). Silicate-requiring diatoms, which are one of the large-sized phytoplankton groups and have an important role in the biological pump, are responsible for ~75 % of the annual primary production in the Southern Ocean (Tréguer et al., 1995). Therefore, silicate availability is an important factor when considering the enhancement of export production via OIF experimentation. As SOIREE and EisenEx were performed to the south of the PF under intermediate silicate concentration (~5–25 μM) conditions (Boyd et al., 2000; Gervais et al., 2002) (Fig. 4c; Fig. 4a for experiment locations), the interaction between silicate availability and iron addition was not clearly verified. To elucidate this issue, two OIF experiments were conducted during January–February of 2002 in two distinct regions: The Southern Ocean iron experiment-north (SOFeX-N) and -south (SOFeX-S) of the PF (Coale et al., 2004; Hiscock and Millero, 2005) (Table 1).

To measure biologically driven gas fluxes (e.g., $CO_2$, dimethylsulfide, CO, $N_2O$, $N_2$, and $O_2$), the Surface Ocean Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange (SAGE) experiment was conducted during March–April 2004 (15 days) in HNLC sub-Antarctic waters (under low silicate concentration) between subtropical region and the PF (Harvey et al., 2010; Law et al., 2011) (Fig. 4c).

Early OIF experiments had not clearly shown whether artificial OIF could effectively reduce atmospheric $CO_2$ levels through enhancement of the biological pump, i.e., rapid transport of surface organic matter to intermediate/deep waters (Boyd et al., 2007), but the results were interesting enough to spur continued efforts. With the aim of confirming that OIF could increase export production, an experiment known as EIFEX was carried out during February–March 2004 in a PF cyclonic eddy core (Fig. 5). With the intention of finding deep export production, EIFEX was a much longer experiment (39 days), compared to earlier attempts (~21 days) (Smetacek et al., 2012). The Indian and German Atlantic sector iron fertilization experiment (LOHAFEX; 'Loha' is iron in Hindi) was conducted during January–March 2009 (40 days) also in a PF cyclonic eddy at the same latitude with EIFEX, but under low silicate concentration (Fig. 4c) again with the aim of investigating an iron fertilized bloom in the surface layer, deep export carbon production, and biomass converted back into $CO_2$ by bacteria and/or zooplankton (Smetacek and Naqvi, 2010; Martin et al., 2013).

### 2.1.3 OIF in the subarctic North Pacific

A strong longitudinal gradient in aeolian dust deposition (i.e., high dust deposition in the west to low in the east), known as natural OIF, has been found in the subarctic North Pacific (Duce and Tindale, 1991). However, there was little information about differences in phytoplankton biomass and communities along the longitudinal dust gradient (Duce and Tindale, 1991; Moore et al., 2002). To investigate the relationship between phytoplankton biomass/community and this dust gradient, the Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1 (SEEDS-1) was conducted in July–August 2001 (13 days) in the western subarctic gyre using the RV *Kaiyo Maru* (Tsuda et al., 2003, 2005), and the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) was performed in July–August 2002 (25 days) in the in the Gulf of Alaska using the RV *John P. Tully*, *El Puma*, and *Kaiyo-Maru* (Boyd et al., 2004, 2005). The main objective of SERIES was to investigate the duration of phytoplankton blooming (i.e., start to finish) after iron addition. Two years later, SEEDS-2 repeated the experiment in almost same location and season with SEEDS-1 using the RV *Hakuho-maru* and *Kilo Moana* (Tsuda et al., 2007).

### 2.1.4 OIF in the subtropical North Atlantic

To investigate influence of co-limited iron and phosphate on primary production, the *in situ* $PO_4^{3-}$ and $Fe^{2+}$ addition experiment (FeeP) was conducted by adding both phosphate and iron in LNLC region of the subtropical North Atlantic during April–May 2004 (21 days) using two RV *Charles Darwin* and *Poseidon* (Rees et al., 2007).

## 2.2 Environmental conditions prior to iron addition

To investigate initial environmental conditions (~1–7 days before iron addition), physical and biogeochemical properties were determined at the sites of the OIF experiments (Steinberg et al., 1998; Coale et al., 1998; Bakker et al., 2001; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Cisewski et al., 2008; Harvey et al., 2010; Cavagna et al., 2011) (Fig. 6, Table 3 and 4). The OIF experiments were conducted under a wide range of physical conditions in terms of mixed layer depth (MLD) and sea surface temperature (SST).

The MLDs ranged from 10 m (SEEDS-1) to 97.6 m (EIFEX) (Fig. 6c), and were shallower in the equatorial Pacific (mean ± SD = 27.5 ± 2.5 m; SD represents standard deviation) and subarctic Pacific (mean ± SD = 22.7 ± 9.0 m) than in the Atlantic Ocean (FeeP: 40 m) and Southern Ocean (mean ± SD = 56.8 ± 18.9 m). Variation in MLD was highest in the OIF experiments conducted in the Southern Ocean and lowest in those conducted in the equatorial Pacific. MLDs in the experiments performed in the western subarctic Pacific were much shallower in SEEDS-1 (10 m) than in SEEDS-2 (28 m), even though the two experiments were carried out in nearly in the same location and season (Tsuda et al., 2007).

SST at the OIF sites ranged from -0.5 °C (SOFeX-S) to 25.2 °C (IronEx-2) (Fig. 6d). SST was much higher in the OIF experiments conducted in the equatorial Pacific (mean ± SD = 24.1 ± 1.15 °C) and Atlantic Ocean (FeeP: 20.7 °C) than those conducted in the Southern Ocean (mean ± SD = 9.4 ± 2.2 °C) and subarctic Pacific (mean ± SD = 4.9 ± 3.7 °C). Although the two OIF experiments carried out in the equatorial Pacific occurred in different seasons (i.e., IronEx-1: October, IronEx-2: May), the surface physical conditions were quite similar (Steinberg et al., 1998). SOFeX-N/S which were conducted along the same line of longitude in the Southern Ocean exhibited distinct differences in SST; 7.1 °C in SOFeX-N and -0.5 °C in SOFeX-S (Coale et al., 2004). Among the OIF experiments conducted in the Southern Ocean, SAGE carried out in the late summer (late March – early April) had the highest SST (11.5 °C) (Harvey et al., 2010).

Regions for OIF experimentation have usually been selected using preliminary surveys to confirm that the sites were subject to HNLC conditions: high nitrate concentration (>~10 μM) and low chlorophyll-a concentration (<1 mg $m^{-3}$). Nitrate concentrations ranged from 7.9 μM (SAGE) to 26.3 μM (SOFeX-S) (Fig. 6e and Table 3). Among the various OIF HNLC experiment sites, the equatorial Pacific (i.e., IronEx-1 and IronEx-2) had the lowest initial nitrate concentrations (mean ± SD = 10.6 ± 0.2 μM), while the Southern Ocean had the highest (mean ± SD = 21.2 ± 5.8 μM). One exception to the focus on HNLC study sites was the FeeP experiment which took place in the subtropical North Atlantic, a typically LNLC region (nitrate <0.01 μM and chlorophyll-a <1 mg $m^{-3}$) (Fig. 6e and h, Table 3 and 4).

The full range of initial silicate concentrations for all the OIF experiments is expressed in the Southern Ocean where values ranged widely ranged from 0.83 μM (SAGE) to 62.8 μM (SOFeX-S) (Fig. 6f and Table 3). Generally speaking, however, initial silicate concentrations were lower in the equatorial Pacific (mean ± SD = 4.5 ± 0.6 μM) than in the Southern Ocean (mean ± SD = 15.1 ± 20.4 μM) and subarctic Pacific (mean ± SD = 27.3 ± 9.6 μM). Nevertheless, SOFeX-N, SAGE, and LOHAFEX all conducted in the Southern Ocean were representative of very low-silicate HNLC (HNLCLSi) regions with initial silicate concentrations less than 2.5 μM (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).

Phosphate concentrations ranged from 0.01 μM (FeeP) to 1.9 μM (SOFeX-S) (Table 3). Consistent with the World Ocean Circulation Experiment sections and maps (Talley, 2007; Koltermann et al., 2011) which suggest increasing surface and near surface nitrate values from Antarctica equatorward, initial Southern Ocean phosphate concentrations were higher to the south 50° S (mean ± SD = 1.6 ± 0.2 μM) than to the north (mean ± SD = 1.1 ± 0.4 μM). They were also higher in the Atlantic sector (mean ± SD = 1.6 ± 0.2 μM) than in the Pacific sector (mean ± SD = 1.0 ± 0.5 μM). Consistent with both the meridional gradient and the basin differences, IronEx in the equatorial Pacific found generally lower initial phosphate values (<1 μM) similar to those seen by SAGE in the southwest Pacific.

Using continuous shipboard measurement systems, OIF experiments have also observed initial surface partial pressure of $CO_2$ ($pCO_2$) conditions (Wanninkhof and Thoning, 1993; Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Takeda and Tsuda, 2005; Smetacek et al., 2005; Wong et al., 2006; Tsumune et al., 2009; Currie et al., 2011). Initial $pCO_2$ values ranged from 330 ppm (SAGE) to 538 ppm (IronEx-2) (Table 3). Initial $pCO_2$ values were much higher in the equatorial Pacific (mean ± SD = 504.5 ± 33.5 ppm) than those in the Southern Ocean (mean ± SD = 355.3 ± 12.5 ppm) and subarctic Pacific (mean ± SD = 370 ± 16.3 ppm).

As previously mentioned, photosynthetic quantum efficiency (Fv/Fm, where Fm is the maximum chlorophyll fluorescence yield and Fv is the difference between Fm and the minimum chlorophyll fluorescence yield), is widely used to determine the degree to which iron is the limiting nutrient for phytoplankton growth (Fv/Fm ranges from 0 to 1 where conditions are less iron limited condition as Fv/Fm approaches 1) (Boyd et al., 2005). Initial Fv/Fm ratios were less than ~0.3 (Fig. 6g and Table 4) suggesting a tendency for iron limitation. Prior to iron addition, initial chlorophyll-a concentration, measured by fluorometer, ranged from 0.04 mg $m^{-3}$ (FeeP) to 0.9 mg $m^{-3}$ (SEEDS-1) (Fig. 6h and Table 4). However, as was the case for nitrate, compared to all the other OIF experiment sites, FeeP showed unusually low initial chlorophyll-a. The average initial OIF chlorophyll-a concentration was 0.43 ± 0.27 mg $m^{-3}$. Prior to the OIF experiments, except in SEEDS-1, SOFeX-S, and EIFEX where the diatoms were dominated by micro-plankton (20–200 μm), phytoplankton communities were dominated by pico-plankton (0.2–2.0 μm) and nano-plankton (2.0–20 μm) (Coale et al., 1998; Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010; Tsuda et al., 2007; Martin et al., 2013).

**2.3 Tracing the effects of iron addition**

Iron(II) and sulfate aerosols are ubiquitous in the atmosphere, and therefore iron-sulfate ($FeSO_4 \cdot H_2O$), a common form of combined iron that enters the ocean environment via dust deposition, has been frequently regarded as a bioavailable iron source for glacial periods (Zhuang et al., 1992; Zhuang and Duce, 1993; Spolaor et al., 2013). In addition, iron-sulfate is a common inexpensive agricultural fertilizer that is relatively soluble in acidified seawater (Coale et al., 1998). Therefore, OIF experiments have been carried out by releasing commercial iron-sulfate dissolved in acidified seawaters into moving ship propeller wash (Fig. 5).

The patch size fertilized by the first iron addition varied from 25 $km^2$ (e.g., FeeP; iron addition of 1840 kg) to 300 $km^2$ (e.g., LOHAFEX; iron addition of 2000 kg) (Boyd et al., 2007; Martin et al., 2013) (Table 1 and Fig. 6a and b). In general, background dissolved iron concentrations in the ocean environment are <0.2 nM. During the OIF experiments, dissolved iron concentrations increased to ~1.0–4.0 nM and decreased to background concentrations within days (Table 1). The fast decrease in dissolved iron concentrations indicates that iron-sulfate was transformed chemically into a solid form that readily sticks to other substances. This process occurs more rapidly in warmer waters (ACE CRC, 2015). Therefore, except for the single iron addition experiments of IronEx I, SEEDS-1, and FeeP (Martin et al., 1994; Tsuda et al., 2005; Rees et al., 2007), to maintain an iron-fertilized patch, most of the OIF experiments conducted multiple iron additions at the patch centre. These multiple addition experiments included: (2 additions) EIFEX, SERIES, SEEDS-2, LOHAFEX (Boyd et al., 2005; Smetacek et al., 2012; Martin et al., 2013), (3 additions) IronEx-2, EisenEx, SOFeX-N (Coale et al., 1996; Gervais et al., 2002; Coale et al., 2004;

Nishioka et al., 2005), and (4 additions) SOIREE, SOFeX-S, SAGE (Boyd and Law, 2001; Coale et al., 2004; Harvey et al., 2010) (Table 1).

To trace the iron-fertilized patch, OIF experiments used a combination of biogeochemical-based and physical-based approaches. In biogeochemical approaches, the OIF experiments (except EIFEX) used sulfur hexafluoride ($SF_6$) artificially added as a chemical tracer (Martin et al., 1994; de Baar et al., 2005). $SF_6$ is useful for investigating physical mixing and advection-diffusion processes in the ocean environment due to its low solubility, nontoxicity, and biogeochemically inert characteristics (Law et al., 1998). Injected $SF_6$ concentrations were continuously monitored using gas chromatography with an electron capture detector system (Law et al., 1998; Tsumune et al., 2005). Usually only one $SF_6$ injection was necessary as background levels are generally extremely low in the ocean (<1.2 fM; f: femto-, $10^{-15}$) (Law et al., 1998; Law et al., 2006; Martin et al., 2013), however, in the SAGE experiment with higher mixing and lateral dilution, there were three injections (Harvey et al., 2010). Underway sampling systems, measuring biogeochemical parameters such as Fv/Fm ratio, $pCO_2$, and chlorophyll fluorescence, were also used in the fertilized patch as alternative means of following the patch (Gervais et al., 2002; Boyd et al., 2005; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012).

In physically based approaches, surface-drifting buoys equipped with Array for Real-time Geostrophic Oceanography (ARGO) and Global Positioning System (GPS) sensors have been used to map moving fertilized patches in space and time (Coale et al., 1998; Boyd and Law, 2001; Law et al., 2006; Martin et al., 2013). Buoy position can be transmitted to the ship every 5–10 min. The NASA airborne oceanographic lidar aircraft have also been employed to assess the large-scale effects of iron addition on surface chlorophyll in the fertilized patch compared to surrounding regions (Martin et al., 1994).

### 2.4 Biogeochemical responses

The biogeochemical responses to a wide range of iron addition (350–4000 kg) via OIF experiments in the HNLC regions were surveyed over periods ranging from 10–40 days (Table 1 and Fig. 6b). The initial response was a rapid increase of Fv/Fm ratio generally observed within the first 24 hours after iron addition. This was not the case in SEEDS-1 and SEEDS-2 where a detectable increase was observed 3–5 days later. The maximum post-iron-addition Fv/Fm ranged from 0.31 (SEEDS-1) to 0.65 (SOIREE and SOFeX-S) and Fv/Fm generally reached values of 0.5 or greater (Table 4 and Fig. 7a). The increase in Fv/Fm ratio after iron addition suggests that phytoplankton response to iron enrichment is prompt, and results support the hypothesis that natural phytoplankton growth in these HNLC regions is iron-limited (Boyd and Abraham, 2001; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2005; Barber and Hiscock, 2006; Tsuda et al., 2007; Peloquin et al., 2011; Croot et al., 2008; Martin et al., 2013).

Depletion of macro-nutrients in fertilized patches provides indirect evidence that phytoplankton growth in surface waters is driven by iron fertilization (Boyd and Law, 2001). Significant nitrate uptake (i.e., $\Delta$Nitrate = $[NO_3^-]_{post\text{-}fertilization}$ – $[NO_3^-]_{pre\text{-}fertilization}$ <0) occurred in all the OIF experiments, except SAGE (Table 3 and Fig. 7b) (Martin et al., 1994; Boyd et al., 2000; Hiscock and Millero, 2005; Law et al., 2011). Negative ΔNitrate ranged from -0.7 μM in the equatorial IronEx1 experiment to -15.8 μM in SEEDS-1. However, in SAGE, concentrations of macro-nutrients in the iron fertilized patch exceeded the initial concentrations (i.e., ΔNitrate >0) due to the physical processes such as deepened MLD and lateral advection of high nutrient waters (Table 3 and Fig. 7b) (Law et al., 2011).

Changes in surface water chlorophyll-a concentrations are a direct indication of the effect of iron addition on phytoplankton growth (Fig. 7c). Generally, chlorophyll-a concentrations increased substantially 2- to 20-fold with max values of ~0.1 mg m$^{-3}$ (FeeP) to 22 mg m$^{-3}$ (SEEDS-1) (Fig. 7c and Table 4) when nitrate concentrations sharply decreased from 3–5 days after iron addition (Tsuda et al., 2003; Coale et al., 2004; Boyd et al., 2004; Tsuda et al., 2007; Peloquin et al., 2011; Smetacek et al., 2012). SEEDS-1 and SEEDS-2, performed under similar conditions, presented similar initial chlorophyll-a concentrations (0.8 mg m$^{-3}$), but their responses to iron addition were different. Iron-stimulated max chlorophyll-a concentration in SEEDS-2 (~2.5 mg m$^{-3}$) was much lower than those of SEEDS-1 (~22 mg m$^{-3}$) (Tsuda et al., 2007). Satellite observations were also used to spatially and temporally map OIF phytoplankton response (Boyd et al., 2000; Coale et al., 2004; Boyd et al., 2005; Westberry et al., 2013). Spatial changes in chlorophyll-a concentration as a result of iron addition were detected in SOFeX-N/S using Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images. The chlorophyll-a image at ~28 days after iron addition in the SOFeX-N showed a phytoplankton bloom distribution resembling a long thread shape (~1.0 mg m$^{-3}$), while chlorophyll-a image at ~20 days in the SOFeX-S suggested a somewhat broader bloom pattern (~0.4 mg m$^{-3}$) (Fig. 7d) (Westberry et al., 2013).

However, influence of iron addition on the phytoplankton growth covers from surface to euphotic depth as added iron is mixed within the mixed layer by physical processes (Coale et al., 1998). Although maximum chlorophyll-a concentrations during SEEDS-1 (~22 mg m$^{-3}$) were much higher than EIFEX (~3.2 mg m$^{-3}$), mixed layer integrated chlorophyll-a concentrations were similar to ~250 mg m$^{-2}$. There were distinct differences between mixed layer integrated chlorophyll-a concentration and surface chlorophyll-a concentration. Therefore, during previous OIF experiments, to quantify the exact changes in phytoplankton biomass to iron addition, it would be important to detect the change in integrated primary productions within MLDs. Associated with the OIF-induced phytoplankton blooms, the magnitude of primary productivity integrated from the surface to euphotic depth in iron fertilized patches also became significantly elevated compared to initial levels (i.e., $\Delta PP = PP_{post\text{-}fertilization} - PP_{pre\text{-}fertilization}$, where PP is primary productivity). Increases in ΔPP ranged from 360 mg C m$^{-2}$ d$^{-1}$ (SAGE) to 1800 mg C m$^{-2}$ d$^{-1}$ (IronEx-2) with maximum values of 790 mg C m$^{-2}$ d$^{-1}$ (EisenEx) to 2430 mg C m$^{-2}$ d$^{-1}$ (IronEx-2) (Fig. 7e and Table 4). As a result of increased ΔPP, drawdown of $pCO_2$ (negative $\Delta pCO_2$: air→sea) was enhanced during the all OIF experiments except SAGE (Fig. 7f). In SAGE, physical mixing caused an increase in macro-nutrients (positive ΔNitrate, Fig. 7b), which resulted in a reversed $pCO_2$ pattern (positive $\Delta pCO_2$: sea→air) (Currie et al., 2011). The largest $\Delta pCO_2$ change occurred in SEEDS-1 conducted in the subarctic North Pacific (Fig. 7f). It also produced the largest ΔNitrate and the greatest chlorophyll increase (Fig. 7b and c) (Tsuda et al., 2003; de Baar et al., 2005). Overall, OIF $\Delta pCO_2$ reductions ranged from -6 ppm (SEEDS-2) to -130 ppm (SEEDS-1) (Table 3 and Fig. 7f), and were associated with DIC decreases of 6 μM (IronEx-1) to 58 μM (SEEDS-1) (Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Boyd et al., 2007; Berg et al., 2011; Currie et al., 2011).

Using both microscopes and high performance liquid chromatography pigment analysis, changes in phytoplankton community effected by iron addition were also investigated. During IronEx-2, SOIREE, EisenEx, SEEDS-1, SOFeX-S, SERIES, and EIFEX, the dominant phytoplankton community tended to shift from pico- and nano-plankton to micro-plankton, resulting in diatom-dominated phytoplankton blooming, a key component for biological pump enhancement (Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010). However, there were no observations on taxonomic shift toward diatom-dominated phytoplankton communities in other OIF experiments (Coale et al., 1998; Coale et al., 2004; Rees et al., 2007; Tsuda et al., 2007; Peloquin et al., 2011; Martin et al., 2013). As noted above, the SEEDS-1 and SEEDS-2 experiments were carried out under similar ocean conditions. Nevertheless, SEEDS-2, which resulted in a minimal increase in chlorophyll-a (<3 mg m$^{-3}$), was also subject to extensive copepod (meso-zooplankton; 200–2000 μm) grazing (~5 times greater than in SEEDS-1) and therefore did not produce a prominent diatom bloom (Tsuda et al., 2007).

## 2.5 Assessment of export carbon flux

Early OIF experiments showed that iron addition stimulates the first step of the biological pump, promotion of phytoplankton growth. To determine whether the second step of the biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, the export flux of particulate organic carbon (POC) has been estimated using, either together and/or individually, chemical tracers such as natural radiotracer thorium-234 ($^{234}$Th; half-life = 24.1 days) and the stable carbon isotope of particulate organic matter ($^{13}C_{org}$), free-drifting sediment traps, beam-transmissometers, and underwater video profilers (UVP) (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

The $^{234}$Th isotope has a strong affinity for suspended particles, and the extent of $^{234}$Th removal in the water column is indicative of the export production below the euphotic zone associated with surface primary productivity (Buesseler, 1998). In IronEx-2, which was the first OIF experiment in which POC flux was estimated, surface values were calculated from the so-called $^{234}$Th activity balance method (Bidigare et al., 1999). The $^{234}$Th deficiency of the surface ocean (25 m) during IronEx-2 was evident in the iron-fertilized patch, indicating iron-stimulated export production (Table 5). However, there were no $^{234}$Th observations conducted in the unfertilized patch for comparison and nor were there observations to estimate downward POC export to the deep ocean (Bidigare et al., 1999).

SOIREE was first study to quantify downward export processes to the deep Southern Ocean using a comprehensive suite of methods such as $^{234}$Th and $^{13}C_{org}$ estimates derived from high volume pump sampling, free-drifting sediment trap deployments, and beam transmissometer (Nodder and Waite, 2001). However, no measurable change in carbon export was observed in response to iron-stimulated primary production during the 13-day occupation of the SOIREE (Fig. 8b and Table 5) (Charette and Buesseler, 2000; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001). For EisenEx, $^{234}$Th observations showed no differences between in-patch and outside-patch export rates (U. Riebesell et al., unpublished manuscript). Although POC export fluxes in the surface layer (50 m) changed from 374 to 1000 mg C $m^{-2}$ $d^{-1}$ with the formation of an iron-induced phytoplankton bloom during SEEDS-1, there was no significant increase in POC export flux measured from the drifting sediment trap deployments at 200 m during the observation period (Aono et al., 2005). These results suggest that most of the POC stayed in the surface mixed layer, that is, did not extend down to 200 m (Takeda and Tsuda, 2005).

For SOFeX-N/S, enhanced POC fluxes out of the mixed layer after iron enrichment were obtained from $^{234}$Th observations (SOFeX-S) and free-profiling robotic Lagrangian carbon explorers with transmissometers (SOFeX-N) (Bishop et al., 2004; Buesseler et al., 2005). However, the absolute magnitude of these flux increases was similar to those for natural blooms in the Southern Ocean. During SERIES and SEEDS-2, which allowed comprehensive time-series measurements of the development and decline of an iron-stimulated bloom, POC fluxes defined by the sediment trap deployment showed temporal variation with development and decline phases in the fertilized patch (Boyd et al., 2004; Aramaki et al., 2009). These results suggested that only small part of the decrease in mixed layer POC was subsequently captured by the trap and losses of POC flux were mainly governed by bacterial remineralization and mesozooplankton grazing (Boyd et al., 2004; Tsuda et al., 2007). For SAGE and

LOHAFEX under Si limitation in the Southern Ocean (Fig. 4c and 6f), there was no detection for fertilization-induced export by any method (Table 5) (Peloquin et al., 2011; Martin et al., 2013).

In contrast to other previous experiments, EIFEX provided clear evidence that the carbon export was stimulated by artificial iron addition (Jacquet et al., 2008). During EIFEX, initial the export flux, estimated using $^{234}Th$ in the upper 100 m of the fertilized patch, was 340 mg C $m^{-2}$ $d^{-1}$ (Fig. 8a and Table 5) (Smetacek et al., 2012). This value remained constant for 25 days after iron addition. Then, between 30 and 36 days after iron addition, a massive increase in export flux as high as 1692 mg C $m^{-2}$ $d^{-1}$ was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Fig. 8a and Table 5). The profiling transmissometer with high-resolution coverage also showed that there was an increase in exported POC below 200 m after 28 days. At least half of iron-induced biomass sank far below to a depth of 1000 m with tenfold higher sinking rate (500 m $d^{-1}$), comparable to the initial conditions, via aggregate formations of diatom species, '*Chaetoceros dichaeta'* (Smetacek et al., 2012). That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments, suggesting that the effectiveness of iron addition on this component of the biological pump remains a question that needs to be resolved in future OIF experiments (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

### 2.6 Significant results and limitations in previous OIF experiments

To understand how various physical and biogeochemical properties response to artificial iron addition in HNLC regions, previous OIF experiments have been conducted with various objectives (Table 2). These various objectives have contributed to develop ideas/approaches to find optimal conditions that have potential capacity to efficiently sequester carbon (Smetacek et al., 2012). To test iron hypothesis, initial artificial OIF experiments (e.g., SEEDS-1 and IronEx-2) have focused on whether iron supply limits phytoplankton growth in HNLC regions and have confirmed increases in phytoplankton biomass by showing maximum drawdown of $pCO_2$ by 130 ppm in SEEDS-1 and in primary production by 1800 mg C $m^{-2}$ $d^{-1}$ in IronEx-2 (Fig. 7e and f) (de Baar et al., 2005; Boyd et al., 2007). Massive phytoplankton bloom was due to rapid increase in diatom production (Coale et al., 1996; Boyd et al., 2000). There were multiple efforts to detect deep export production from surface iron-induced massive phytoplankton bloom, as the second step of iron hypothesis (Bidigare et al., 1999; Charette and Buesseler, 2000; Coale et al., 2004; Smetacek et al., 2012). EIFEX only showed significant export carbon to deep layer of 3000 m by aggregate formation with highly fast sinking rates (Table 5) (Smetacek et al., 2012). Despite highly increased phytoplankton production in the mixed layer by OIF experiments (e.g., SEEDS-1, SOFeX-N/S, SERIES, and SEEDS-2), export production was relatively low. Thus, the study focus was on high bacterial remineralization (SERIES) and/or grazing pressure (SEEDS-2) in the upper water columns (Boyd et al., 2004; Tsuda et al., 2007). Relatively slight increase in primary production to iron addition (~500 mg C $m^{-2}$ $d^{-1}$) occurred in SAGE and LOHAFEX experiments, which were designed to investigate biogeochemical response to iron addition in very low silicate concentrations (<~2 nM) (Table 2) (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).

## 3 Present: OIF debates and considerations including possible side effects and international law

### 3.1 Environmental side effects

OIF has been proposed as one potential way (*a.k.a.* 'Carbon Capture Storage') of rapidly and efficiently reducing atmospheric $CO_2$ levels at relatively minimal cost (Buesseler and Boyd, 2003). Over the past 25 years, controlled OIF experiments have illustrated that substantial increases in phytoplankton biomass can be instigated in HNLC regions through iron addition that results in the drawdown of DIC and macronutrients (de Baar et al., 2005; Boyd et al., 2007; Smetacek et al., 2012; Martin et al., 2013). However, the effectiveness of enhancement in this export production, which results in a net transfer of $CO_2$ from the atmosphere to the ocean intermediate/deep layer (i.e., 'biological pump'), is not yet fully understood or quantified as it appears to vary with region, season, and as yet unknown factors (Smetacek et al., 2012). Therefore, it is uncertain whether OIF has the potential to sequester $CO_2$ at a significant rate (~1 Gt of $CO_2$ per year). In the meantime, there are possible environmental side effects in response to iron addition, such as production of greenhouse gases (e.g., $N_2O$ and $CH_4$) (Lawrence, 2002; Liss et al., 2005; Law, 2008), development of hypoxia/anoxia in water column (Sarmiento and Orr, 1991), and toxic algal blooms (e.g., *Pseudo-nitzschia*) (Silver et al., 2010; Trick et al., 2010), that have been seen and should be addressed before artificial OIF is conducted. These OIF experiment side-effects may themselves effect climate and ecosystem changes that have unexpected negative outcomes (Fuhrman and Capone, 1991). Therefore, it is not surprising that the OIF validation and usefulness has been a subject of debate (Williamson et al., 2012).

OIF experiments have measured climate-relevant gases (i.e., $N_2O$, $CH_4$, dimethylsulfide, and halogenated volatile organic compounds) that are produced by biological activity and/or photochemical reaction (Liss et al., 2005) to investigate change before and after iron addition. $CH_4$ has been considered to be relatively low risk as most of the $CH_4$ formed in the ocean is used as energy source for microorganisms and is converted to $CO_2$ before reaching to the sea surface (Smetacek and Naqvi, 2008; Williamson et al., 2012). Measurements of dissolved $CH_4$ during the SOFeX-N showed slightly elevated concentrations at less than 1 % (Wingenter et al., 2004). Simulated Southern Ocean large-scale iron fertilization has suggested that enhancement of $CH_4$ emission would offset only <1 % of the resulting carbon sequestration (Oschlies et al., 2010). On the other hand, the ocean is already a significant source for atmospheric $N_2O$, which has relatively the long lifetime (~110 years) in the atmosphere and has a global warming potential about 300 times greater than $CO_2$ (Forster et al., 2007). Therefore, any enhancement of biological production that might enhance $N_2O$ emission could work to increase atmospheric greenhouse gas levels rather than decrease them (Bange, 2006). During the SOIREE experiment, a significant increase (~7 %) in mean $N_2O$ saturation in the pycnocline of the fertilized patch was associated with increased phytoplankton biomass (Law and Ling, 2001). Measurements of $N_2O$ saturation during SERIES also showed increases of 8 % at 30–50 m, which were coincident with the accumulation of ammonium and nitrite attributable to bacterial remineralization (Boyd et al., 2004; Law, 2008). Model estimates suggested that potential $N_2O$ production on longer timescales (6 weeks) would subsequently offset by 6–12 % increased carbon reduction benefits resulting from remineralization of additional carbon fixed during SOIREE (Law and Ling, 2001). This estimate is in the same range as the $N_2O$ offset of 6–18 % suggested by an earlier modeling study (Jin and Gruber, 2003) and the 5–9 % suggested by a more recent modeling study investigating the effectiveness of long-term and large-scale Southern Ocean OIF (Oschlies et al., 2010). Complicating the story, however, excess $N_2O$ was not found after iron addition during EIFEX, which showed significant vertical export with formation of rapidly sinking aggregate (Walter et al., 2005; Law, 2008). An explanation for the absence of $N_2O$ accumulation below EIFEX patch might be limited bacterial remineralization by rapid export to the seafloor (Walter et al., 2005).

Unlike $N_2O$ emissions which have the potential to offset the effectiveness of OIF, dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, may contribute to the homeostasis of the earth's climate by countering warming from increasing $CO_2$ (Charlson et al., 1987). The DMS response to iron addition was measured during all OIF experiments. In equatorial Pacific and Southern Ocean, DMS increased, but in the subarctic Pacific, it remained constant or decreased (Lawrence, 2002; Boyd et al., 2007). Significant short-term increases in DMS production were found in IronEx-2, SOIREE, EisenEx, and SOFeX-N (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). The maximum DMS production observed was a 6.5-fold increase after iron addition during SOIREE (Turner et al., 2004). Similarly, a 5-fold enhancement of DMS was observed during SOFeX-N. Estimates derived by extrapolation of SOFeX-N DMS results to the Southern Ocean OIF experiment with 2 % areas suggested that iron fertilization would enhance DMS production by 20 %, which would lead to a 2 °C decrease in air temperature over the Southern Ocean (Wingenter et al., 2007). Interestingly, there were no significant changes in DMS production after iron addition in SEEDS-1 and SEEDS-2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). Contrast to SEEDS-1 and SEEDS-2, DMS production decreased in SERIES experiment due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production. It is therefore clear that there are yet unknown factors affecting iron-induced DMS response, as it appears that OIF could be a significant source of DMS production in Southern Ocean and yet induce a DMS sink in subarctic Pacific. These results indicate that further observation-based and modeling studies are required to determine different features from place to place (Law, 2008).

Halogenated volatile organic compounds (HVOCs, such as $CH_3Cl$, $CH_3Br$, and $CH_3I$), well known for their ability to destroy ozone in the lower stratospheric ozone and marine boundary layer (Solomon et al., 1994), were also measured during the OIF experiments (Wingenter et al., 2004; Liss et al., 2005). During SOFeX-N experimentation, iron addition results for HVOC were complicated: $CH_3Cl$ concentrations remained unchanged; $CH_3Br$ concentrations increased by ~14 %; and while generally $CH_3I$ concentrations decreased by ~23 % (Wingenter et al., 2004). $CH_3I$ concentrations increased 2-fold in EisenEx (Liss et al., 2005). Therefore, as the DMS response above, further study is needed to understand the complexity of the HVOC response.

Decomposition of iron addition-enhanced biomass may cause decreased oxygen concentrations in the subsurface waters (Williamson et al., 2012). Although mid-water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF-induced oxygen depletion may occur as increased downward carbon exports elevate microbial respiration (Fuhrman and Capone, 1991). Early studies using box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). However, more sophisticated and realistic models associated with OIF-induced oxygen changes in water columns showed well-oxygenated conditions without developing anoxic conditions (Oschlies et al., 2010; Keller et al., 2014).

The changes of phytoplankton community composition after iron addition discussed in Section 2.4 may also have unintended consequences, in particular, toxin production (Silver et al., 2010; Trick et al., 2010). Some OIF experiments (including IronEx-2, SOIREE, EisenEx, and SOFeX-N/S) generated large blooms of diatoms dominated by pennate diatoms belonging to the genus '*Pseudo-nitzschia*' (de Baar et al., 2005; Trick et al., 2010). Some species of the genus '*Pseudo-nitzschia*' have the capacity to produce the neurotoxin domoic acid (DA) that is known to detrimentally affect marine ecosystems. For example, during IronEx-2 and SOFeX-S, high cell abundances of '*Pseudo-nitzschia*' (106 and 105 cells $l^{-1}$, respectively) combined with moderate DA quotas (0.05 and 1 pg DA $cell^{-1}$, respectively) produced toxin levels as high as 45 ng DA $l^{-1}$ in IronEx-2 and 220 ng DA $l^{-1}$ in SOFeX-S; i.e., toxin levels that is able to cause certain damages to marine communities in coastal waters (Silver et al., 2010). However, no DA was found during EisenEx, even though diatom species of the genus '*Pseudo-nitzschia*' were dominant numerically (Gervais et al., 2002; Assmy et al., 2007).

The direct and indirect environmental consequences of OIF remain unresolved due to inconsistent, highly uncertain outcomes (Williamson et al., 2012; Johnson and Karl, 2002; Chisholm et al., 2001), suggesting that we haven't yet reached to a conclusion as to whether OIF is a feasible carbon removal strategy (Boyd et al., 2007). Therefore, evaluation and prediction are paramount. It continues to be a valuable exercise to seek answers to scientific questions about the effectiveness of OIF as a means of reducing atmospheric $CO_2$ as well as to quantify possible OIF side effects. In particular, potential trace gas emissions such as $N_2O$ and DMS, which are influenced by the remineralization of sinking particles that follows OIF-induced blooms, are important to understand. They can directly and indirectly modify the desired carbon sequestration effectiveness and they can do so both positively and negatively. Therefore, monitoring of $N_2O$ and DMS to evaluate the effectiveness of OIF as a geoengineering approach is essential.

### 3.2 International law of the sea to OIF

To date, assessment of the effectiveness of OIF has been limited by the small area of the fertilized patches (25–300 $km^2$) used in the experiments (Fig. 6a). Patch sizes have been limited in part due to the time and expense of comparing fertilized and unfertilized areas (ACE CRC, 2008). Nevertheless, as these small-scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric $CO_2$ levels, physical/biogeochemical/ecological models and natural (long-term) iron fertilization experiments have been studied in an effort to overcome some of the limitations of short-term iron-addition experiments and to predict the effectiveness of long-term and large-scale fertilization (Aumont and Bopp, 2006; Blain et al., 2007; Denman, 2008; Pollard et al., 2009). Earlier simplistic global biogeochemical models suggested that massive fertilization could draw down atmospheric $CO_2$ by as much as 107 ppm in 100 years (Joos et al., 1991; Peng and Broecker, 1991; Sarmiento and Orr, 1991; Kurz and Maier-Reimer, 1993). Recent global models with a more realistic ecosystem and biogeochemical cycles predict values closer to 33 ppm drawdown in atmospheric $CO_2$. These results suggest that the amount of carbon sequestration resulting from OIF would represent only a modest offset, a contribution less than 10 % for the range of IPCC future emissions scenarios (Aumont and Bopp, 2006; Denman, 2008). Natural OIF experiments also showed much higher carbon sequestration rates than the small-scale OIF experiments (Morris and Charette, 2013), suggesting that there may be scaling or timing issues in the smaller experiments that preclude simple scaling-up as a prediction tool (see discussion in Section 4). For this reason, several commercial companies (e.g., GreenSea Venture and Climos, http://www.greenseaventure.com; http://www.climos.com) have been promoting large-scale commercial OIF experiments as a climate mitigation strategy and a means to gain carbon credits (Chisholm et al., 2001; Buesseler and Boyd, 2003). However, this effort has not been able to move forward because we have little knowledge about the potential magnitude of possible side effects related to large-scale geoengineering OIF. It remains difficult to extrapolate findings from the small-scale OIF experiments because the environmental/ecosystem side effects from these miniature studies are themselves quite variable and not yet clearly understood. However, presently available studies do indicate that the known side effects from small-scale studies are themselves small-scale. It therefore seems reasonable that we should continue to undertake small-scale studies to better assess these risks and so lay the groundwork for evaluating the potential efficacy and impacts of large-scale OIF as a geoengineering solution to anthropogenic change.

With potential risks and benefits of OIF, there have been legal issues surrounding OIF raised to support the further study and increase understanding of OIF (Williamson et al., 2012). At present, large-scale and/or commercial OIF experiments are banned by international regulation. The international Convention on the Prevention of Marine Pollution by Dumping of Wastes and

Other Matter (London Convention, 1972) and Protocol to the London Convention (London Protocol, 1996) placed legal restrictions on dumping of wastes and other matter that cause hazard, harm, and damage in the ocean and/or interfere with the marine environment. In 2007, the London Convention & Protocol (LC/LP) scientific groups released a statement of concern about ocean fertilization and recommended that ocean fertilization activities be evaluated carefully to ensure that such operations were not contrary to the aims of the LC/LP. Under the LC/LP, commercial activities are prohibited, and only 'small-scale' legitimate scientific research in 'coastal waters' is allowed (Resolution LC-LP.1 (2008), 2008). LC/LP also developed an assessment framework for scientific ocean fertilization research to be applied on a case-by-case basis founded on the agreed definition and compliance with the aims and objectives of Resolution LC-LP.1 (2008) (Fig. 9) (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). This framework demands preliminary scientific research to get a permission for OIF experimentation as transparent/reasonable scientific rationale/purpose and risk analysis undertaken using parameters such as problem formulation, site selection, exposure assessment, effects assessment, risk characterization, and risk management must be provided (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). Monitoring is also required an integral component of all approved (i.e., legitimate) scientific research activity to assess ecological impacts and to review actual versus intended geoengineering benefits (ACE CRC, 2015). In October 2013, LC/LP categorized artificial ocean fertilization as marine geoengineering, thereby prohibiting operational OIF activities, but enabling OIF scientific research that meets the permit conditions through the environmental assessment framework (Resolution LP.4 (8), 2013).

## 4 Future: Considerations for designing future OIF experiments

Scientific research on OIF has focused on improving our understanding of the effectiveness, capacity, and risks of OIF as an atmospheric $CO_2$ removal strategy. Although the first OIF experiments took place more than twenty years ago, the legal and economic aspects of such a strategy in terms of international laws of the sea and carbon offset markets are not yet clear (ACE CRC, 2015). It is therefore of paramount importance that future OIF experiments continue to focus on the effectiveness and capacity of OIF as a means of reducing of atmospheric $CO_2$, but in doing so should carefully consider iron addition method (i.e., 'How'), tracking methods and measurement parameters (i.e., 'What'), locations (i.e., 'Where'), timing (i.e., 'When'), and duration (i.e., 'How long') to build on the results of OIF experiments, develop our understanding of the magnitude and sources of uncertainties, and in so doing build confidence in our ability to reproduce results.

How: The first consideration for a successful OIF experiment lies in the strategy/approach to maintain added iron within the upper mixed layer. During the first OIF experiment, IronEx-1, the patch was fertilized with acidified iron(II) sulfate according to the target concentrations of 3.6 nM because iron enrichment bottle incubation experiments performed in deck board incubators using ocean water suggested maximum phytoplankton growth rates in response to iron additions of 1–2 nM (Fitzwater et al., 1996). However, subject to horizontal dispersion, concentrations of iron added in the open ocean rapidly decreased from 3.6 nM to 0.25 nM in just four days. Further, the magnitude of the open ocean biogeochemical response was less than bottle enrichment experiments suggested (Coale et al., 1998). Seeking to sustain enhanced iron concentrations in patches, since IronEx-2, the technique of applying repeated (2 to 4) iron infusions has been used in all OIF experiments except SEEDS-1 and FeeP (de Baar et al., 2005; Boyd et al., 2007). Like IronEx-1, SOIREE showed that losses in dissolved iron after the first iron infusion rapidly increased due to horizontal dispersion, and also noted loss due to oxidation of the additional iron(II) to iron(III) (Bowie et al., 2001). However, SOIREE demonstrated that four additions of iron with intervals of about 3 days led to a persistent elevation of both dissolved and particulate iron within the mixed layer at the end of the experiment through fast reduction combined with an increase in the concentration of iron-binding ligands after multiple infusions. Both EIFEX and SOFeX-S also found that multiple iron(II) infusions allowed iron to persist in the mixed layer longer than its expected oxidation times. They determined that the relatively low oxidation rates were related to a combination of photochemical production, slow oxidation, and possibly organic complexation (Croot et al., 2008). Blain et al. (2007) explained that the higher carbon sequestration effectiveness of natural OIF experiments compared to artificial OIF experiments partly resulted from the slow and continuous iron addition that occurs in the natural environment. Short-term infusions of large amounts of iron tend to lead the substantial loss of artificially added iron. Therefore, to increase ration of the amount of carbon flux exported to the amount of iron supplied, multiple additions of iron are more efficient.

What: The second consideration for a successful OIF experiment is effective tracing of fertilized patch including detection of carbon sequestration (Buesseler and Boyd, 2003) and monitoring of possible side effects. OIF side effects include emission of climate-relevant gases such as $N_2O$ and DMS that directly contribute to warming and cooling of the environment, respectively (Law, 2008). During IronEx-1, the fertilized patch was subsequently traced with large variety of physical-biogeochemical techniques and parameters such as GPS and ARGO equipped drifting buoys, $SF_6$, Fv/Fm ratio, $pCO_2$, and chlorophyll fluorescence using underway sampling systems, and satellite images (Martin et al., 1994; Coale et al., 1998). As IronEx-1 provided potential evidence to support Martin's iron hypothesis by showing an increase in phytoplankton bloom with iron enrichment, many subsequent OIF experiments adopted the tracing methods introduced by IronEx-1, and were similarly able to detect environmental changes through the observation of both physical and biogeochemical parameters before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012). Carbon export fluxes can be detected using $^{234}Th$, $^{13}C_{org}$, free-drifting sediment traps, beam-transmissometers, and UVPs (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). In particular, it is possible to evaluate the temporal evolution of iron-induced export carbon fluxes into deeper waters by applying the thorium deficiency method and sediment trap fluxes that were used during previous OIF experiments (Table 5). Because of their high vertical resolution, the profiling transmissometer, the UVP with its camera that photographs particles, and transmissometers riding on profiling autonomous floats could provide a record of temporal evolution in POC stocks through successive depth layers once calibrated using POC measurements (Smetacek et al., 2012; Martin et al., 2013). Future OIF experiments could benefit from these technological advances so as to more efficiently trace carbon export flux at higher vertical and temporal resolution than has been done in the past. Nevertheless, the application of multiple methods including trap fluxes and $^{234}Th$ deficiency to provide relatively direct flux estimates combined with autonomous profilers with their higher resolution would produce the best results.

Where: The third consideration for a successful OIF experiment is the location selection. The dominance of diatoms in phytoplankton communities plays major role in biological pump efficiency because some species of diatom rapidly sink in aggregate formations and have high accumulation rates of heavily silicified frustules (Tréguer et al., 1995). On the other hand, mesozooplankton (i.e., copepods) graze on large diatoms and so are a major limiting factor in diatom production (Coale et al., 2004; Tsuda et al., 2007). Therefore, to obtain the greatest possible carbon export flux in response to iron addition, OIF experiments should be designed in regions with high silicate concentrations and low copepod abundances. In selecting sites for iron fertilization, it is also important to isolate the iron-fertilized patch from the surrounding unfertilized waters to easily and efficiently observe iron-induced changes (Coale et al., 1996). Ocean eddies provide an excellent setting for OIF experimentation as they have physically rotating water column structures, that naturally tend to isolate interior waters from the surrounding waters. Mesoscale eddies range from 25–250 km in diameter and maintain their characteristics for 10–100 days after formation (Morrow and Le Traon, 2012). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds compared to the surrounding environment and have high vertical coherence, providing ideal conditions for tracing the same water column from the surface to the deep during the experiment (Smetacek and Naqvi, 2008). Iron additions were carried out at the center of eddies in EisenEx, EIFEX, and LOHAFEX conducted in the Southern Ocean (Smetacek, 2001; Smetacek and Naqvi, 2008; Smetacek and Naqvi, 2010; Smetacek et al., 2012). Observations were also made outside the eddy core well away from the iron-fertilized patch to provide similar information about environmental conditions to compare with patch observations. EIFEX showed a clear difference in export carbon flux between waters within the patch and external to the patch (Smetacek et al., 2012). Therefore, finding of an appropriate eddy setting in a study area should be one of the high priority considerations in conducting an OIF experiment (Smetacek and Naqvi, 2008).

When: The fourth consideration for successful OIF experiment is timing including when an experiment starts. Primary production in ocean environment is generally limited by nutrient availability and/or by light availability, often referred to as single- or co-limitation. Primary production in the Southern Ocean, a representative HNLC region, is subject to co-limitation by micro-nutrients (i.e., iron) and light availability (Mitchell et al., 1991). Previous Southern Ocean OIF experiments have been conducted from spring to late summer, and revealed that during this time of year primary production is limited by iron supply rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011). However, the most opportune time, to distinguish phytoplankton blooms increased by iron addition from natural blooms, is during the month of March when natural phytoplankton blooms decline in the Southern Ocean.

How long: The fifth consideration for successful OIF experiment is how long it lasts. Although it has been reported that the periods that phytoplankton blooms have been maintained by OIF have lasted from ~10 to 40 days (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012), it has also been suggested that most OIF experiments did not cover the full response times from onset to termination (Boyd et al., 2005). For example, SOIREE and SEEDS-1, had relatively short observation periods (~13 days) and saw increasing trends in primary production throughout the experiments (Fig. 10a), suggesting that the observation period should have been extended. Furthermore, after the end of SOIREE, ocean color satellite images showed continued high chlorophyll-a concentrations (~1 mg m$^{-3}$) in the iron fertilized patch, which was seen as a long ribbon shape that extended some ~150 km for ~46 days; (~7 weeks) after the initial iron addition (Fig. 10b) (Abraham et al., 2000). This result indicates that short experiment periods may not be sufficient for detecting the full influence of artificial iron addition on primary production (Fig. 8b) (Boyd et al., 2000; Tsuda et al., 2003; de Baar et al., 2005). However, SERIES, SEEDS-2, EIFEX, and LOHAFEX did fully monitor all the phases of the phytoplankton bloom from onset to termination. Among OIF experiments, EIFEX, the second-longest at ~39 days, alone observed iron-induced deep export production between 30 and 36 days after iron addition (Fig. 8a and 10a) (Assmy et al., 2013; Smetacek et al., 2012). Furthermore, long-term observation period covering the later stage of bloom development during natural OIF experiments has made it possible to obtain high carbon sequestration effectiveness (Blain et al., 2007; Pollard et al., 2009). It is therefore important to predict both the necessary time for onset and the time required for the response to run its full course, otherwise it is not possible to quantify the net effect. In addition, to detect the enhancement of the carbon export flux to iron addition, the observation period should last at least 35 to 40 days after iron addition.

In conclusion, to maximize the effectiveness of OIF experiments in the future, we suggest a design that incorporates: ('How') multiple iron additions to 1–2 nM concentration; ('What') multiple means of tracing the fertilized patch including both trap fluxes and/or $^{234}$Th deficiency to obtain direct flux estimates and autonomous platforms such as gliders, equipped with

~~biogeochemical sensors, to obtain high vertical resolution, and monitoring side effect such as $N_2O$ and DMS; ('Where') in an eddy structure with high silicate concentration and low copepod abundance; ('When') e.g., March in the Southern Ocean; ('How long') at least >~35 days.~~

## ~~5. Design for a Korean Iron Fertilization Experiment in the Southern Ocean (KIFES)~~

### ~~5.1 Background - Bransfield Basin~~

~~The last artificial OIF experiment, LOHAFEX was led by scientists from CSIR-National Institute of Oceanography in Goa, Alfred-Wegener Institute for Polar and Marine Research (AWI) in Bremerhaven, and 5 other nations. The German government suddenly halted LOHAFEX just before the departure of RV Polarstern from the port following protests by NGOs and environmentalists against OIF experimentation due to concern about direct and long term side effects of artificial iron fertilization on marine ecosystem. To date, the only OIF experiment with scientific and legal review processes was 'LOHAFEX' conducted in the Southern Ocean. Although people are still worried about side effects of OIF and scientists are still curious about the measurable effects of OIF on the ocean environment, there have been no further intensive investigations to fill the gap between supporters and opponents of OIF as a geoengineering approach since LOHAFEX. There are still many unknowns to be investigated about OIF experiments.~~

~~The paleoclimate team at Korea Polar Research Institute (KOPRI) found geological evidence of intensive organic carbon burial in the sediments (Yoo et al., 2016), which removes atmospheric $CO_2$, in the eastern Bransfield Basin on the Antarctic Peninsula. The diatomaceous ooze layer was well preserved in the buried sediments of the Bransfield Basin (Bahk et al., 2003; Kang et al., 2003; Bak et al., 2015), and represents the fast sinking of diatoms within a short time. Scientists at KOPRI suspect that enhancement of the diatom flux may be related to input of bioavailable iron that controls phytoplankton population by allowing efficient use of surface nutrients. In addition, this unique increase in diatom production, the fast sinking rate of the organic matter, and the remarkably well-preserved organic carbon sediments in this area, suggest the existence of a strong 'biological pump (i.e., significant export production)'. This type of 'bottom-up' approach (see potential for a surface source by looking at the sedimentary evidence) has not been considered in the location selection for previous experiments. Therefore, it is expected that OIF in diatom-dominated eastern Bransfield Basin will be effective for carbon export.~~

~~A science-oriented iron fertilization project, KIFES (Fig. 11), was launched in 2016 with the research funding supported by the Korean Ministry of Oceans and Fisheries. This project was planned mainly by KOPRI with domestic collaborators (i.e., Incheon National University, Inha University, Pusan National University, Hanyang University, and Yeonsei University) and strengthened by international collaborators (i.e., AWI, Institute of Geological and Nuclear Sciences, MIT-WHOI, University of Otago, University of California at Irvine, McMaster University, University of South Florida, Royal Netherlands Institute for Sea Research, and Dalhousie University). The main purpose of KIFES was (1) to evaluate the effectiveness of artificial OIF in terms of atmospheric carbon sequestration (i.e., effectiveness in export production) in the Southern Ocean, (2) to determine the environmental conditions that would maximize effectiveness of artificial OIF, and (3) to reveal short- and long-term side effects derived from a small-scale artificial OIF experiment. Unfortunately, KIFES has lost its present funding source. Nevertheless, optimism prevails that alternative funding will be found at a future date and the following section (5.2) is~~

intended to provide a basic set of design guidelines with expectation that an opportunity to move forward with KIFES will occur in near future.

### 5.2 A plan for the future: KIFES

The KIFES design entails a 5-year project plan. It would model the 'EIFEX' program that found deep carbon by conducting an OIF experiment in an eddy structure. The KIFES project would include a preliminary environmental survey in the eastern Bransfield Basin, a preliminary environmental survey both outside and inside an eddy structure, an OIF experiment, and an assessment of the full KIFES project. In this section, we introduce the major goal, objective, and main tasks of KIFES.

#### 5.2.1 Year one plan

Goal: To gather information about oceanographic conditions in the eastern Bransfield Basin (eBB) including both eddy development and distribution.

Objective: To understand as best we can the physical and biogeochemical oceanography if relevance to the eBB through analysis of earlier data sets and review of published papers.

Main tasks: (1) Database of physical and biogeochemical parameters from previous surveys conducted in the eastern Bransfield Basin; (2) Review of eBB oceanographic conditions using data analysis and references; (3) Design of oceanographic cruise map for the first preliminary eBB survey, based on results from tasks (1) and (2); (4) Analysis of eddy development and distribution using satellite data in the eBB; (5) Preparation of scientific instruments for ocean physical and biogeochemical monitoring; (6) Establishment of an international collaborative OIF network; and (7) KIFES field program proposal preparation for approval of LC/LP.

#### 5.2.2 Year two plan

Goal: First preliminary hydrographic survey to provide a foundational understanding of eBB oceanographic conditions.

Objective: (1) To gain information about oceanographic conditions from in-situ measurements in the eBB; and (2) To provide background information before KIFES experiment.

Main tasks: (1) Using ice breaker RV *ARAON*, field investigation in the eBB of physical and biogeochemical parameters associated with both carbon sequestration as well as OIF side effect (e.g., $N_2O$), based on the first year task results; and (2) Continued preparation of LC/LP proposal.

#### 5.2.3 Year three plan

Goal: Preliminary hydrographic survey outside/inside eddy structure prior to the KIFES experiment.

Objective: To compare oceanographic conditions outside and inside an eBB eddy structure prior to the KIFES experiment.

Main tasks: (1) Detection of an eBB eddy using observations from acoustic Doppler current profilers and satellites; (2) Intensive physical and biogeochemical field investigation both inside and outside an eddy structure; (3) Assessment of physical and biogeochemical properties outside vs. inside an eddy structure prior to KIFES experiment; and (4) Submission of the LC/LP proposal to obtain approval for the KIFES experiment from International Maritime Organization.

**5.2.4 Year four plan**

Goal: KIFES – OIF experiment in an eddy structure (Fig. 11).

Objective: To conduct the eBB artificial OIF experiment.

Main tasks: (1) Execution of the KIFES field campaign, a scientific OIF experiment that will survey the region both inside and outside an eddy structure in the eBB employing underway sampling systems (e.g., such as high frequent $pCO_2$ and Oxygen/Argon ratios), gliders equipped with biogeochemical sensors, sediment traps deployed at multiple depths, sub-bottom profilers, and satellite observations; and (2) Assessment of KIFES carbon sequestration effectiveness and environmental (ocean and atmosphere) side effects.

**5.2.5 Year five plan**

Goal: Integrated assessment of the KIFES project.

Objective: To evaluate whether small-scale OIF experimentation can be an effective tool for detecting the effectiveness of artificially induced export production.

Main tasks: (1) Submission of the KIFES assessment report; (2) Writing and submission of scientific results to international journals; (3) Collection of feedback about the KIFES project from international scientific/oceanographic communities; and (4) Production of a final artificial OIF experiment summary (including Main tasks 1–3).

**5.3 Final Remark**

None of the KIFES scientists has any interest in selling carbon credits by conducting OIF experiments. Rather, KIFES interest lies in the detailed investigation of the biogeochemical effects of artificial iron addition in the Southern Ocean and in the OIF evaluation as one possible geo-engineering method that might be used to mitigate the realities of the climate change effects we face. We look to a future where the KIFES project or one like it becomes a reality so that we may work towards providing a clear answer as to whether or not OIF is promising as a geo-engineering solution. The KIFES project would provide fundamental information and guidelines for future OIF experiments in HNLC regions. In particular, the aforementioned risks and side effects of OIF will be thoroughly investigated so as to belay international concern. And lastly, we emphasize that international cooperation is essential for a project as organizationally and scientifically complex as KIFES, which seeks to improve of our outlook for the Earth's future.

## 6 Summary

To test the Martin's hypothesis, a total 13 artificial OIF experiments for scientific study were conducted in the HNLC regions during the last 25 years. The biogeochemical responses to OIF experiments were observed in the increases of primary production as a result of drawdowns of macro-nutrients and DIC. In most experiments, dominance of phytoplankton group tended to be shifted from small-sized groups to large-sized groups, resulting in diatom-dominated phytoplankton community. However, the effectiveness in export production enhancing ocean biological pump was not clearly confirmed by the OIF experiments, except in one, EIFEX. Likewise, the possible environmental side effects in response to iron addition, such as production of climate-relevant gases, development of hypoxia/anoxia in water column, and toxic algal blooms, were not fully evaluated due to inconsistent outcomes with large uncertainty depending on OIF experiment conditions and settings. In particular, monitoring of $N_2O$ and DMS must be considered in determining effectiveness of OIF as a geoengineering approach because these potential trace gas emissions can directly and indirectly modify carbon reduction benefits resulting from OIF. Therefore, validation and suitability of artificial OIF for mitigation of rapidly increasing atmospheric $CO_2$ levels have been debated for three decades. At present, large-scale or commercial OIF experiments are prohibited by international regulation, so small-scale OIF experimentation with scientific purpose is permitted to understand the effectiveness, capacity, and risks of artificial OIF. To maximize effectiveness of OIF, future OIF experiments should be conducted by carefully considering the major factors such as the methods for iron addition, tracking methods, measurement parameters, location, timing, and experiment duration, under international OIF regulations. Finally, we look to a future the KIFES project or one like it becomes a reality so that we may work towards providing a clear answer as to whether or not OIF is promising as a geo-engineering solution.

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**Table 1.** Summary of OIF experiments; time, location, research vessel, amounts of Fe addition (day of Fe addition from the beginning of OIF experiment), background Fe concentrations, Fe concentrations after Fe additions, tracer, patch size fertilized by first Fe addition, experiments periods, and characteristics of study regions.

| - | Experiment | Time | Location | Research Vessel | Fe (kg) (day) | Initial Fe (nM) | After Fe (nM) | Tracer | Patch size ($km^2$) | Period (days) | Region |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | Oct 1993 | 5° S, 90° W Equatorial Pacific | RV *Columbus Iselin* | ①450 (0) | 0.06 | 3.60 | $SF_6$ | 64 | 10 | HNLC |
| 2 | IronEx-2 | May 1995 | 3.5° S, 104° W Equatorial Pacific | RV *Melville* | ①225 (0)<br>②112 (3)<br>③112 (7) | 0.02 | 2.00<br>1.00<br>1.00 | $SF_6$ | 72 | 17 | HNLC |
| 3 | SOIREE | Feb 1999 | 61° S 141° E Southern Ocean-Australasian-Pacific sector | RV *Astrolab* | ①768 (0)<br>②312 (3)<br>③312 (5)<br>④353 (7) | 0.08 | 3.80<br>2.60<br>2.60<br>2.50 | $SF_6$ | 50 | 13 | HNLC |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | EisenEx | Nov 2000 | 48° S, 21° E<br>Southern Ocean—<br>Atlantic sector | RV *Polarstern* | ①780 (0)<br>②780 (7)<br>③780 (16) | 0.06 | 2.00 | $SF_6$ | 50 | 23 | HNLC |
| 5 | SEEDS-1 | Jul–Aug 2001 | 48.5° N, 165° E<br>North Pacific—<br>Western subarctic gyre | RV *Kaiyo-Maru* | ①350 (0) | 0.05 | 2.90 | $SF_6$ | 80 | 13 | HNLC |
| 6 | SOFeX-N | Jan–Feb 2002 | 56.23° S, 172° W<br>Southern Ocean—<br>Atlantic sector | RV *Revelle*<br>RV *Melville* | ①631 (0)<br>②631 (5)<br>③450 (30) | | 1.20 | $SF_6$ | 225 | 40 | HNLCLSi |
| 7 | SOFeX-S | Jan–Feb 2002 | 66.45° S, 171.8° W<br>Southern Ocean—<br>Atlantic sector | RV *Revelle*<br>RV *Melville*<br>RV *Polar star* | ①315 (0)<br>②315 (4)<br>③315 (7) | | 0.70 | $SF_6$ | 225 | 28 | HNLC |

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| | | | | | ④315 (11) | | | | | |
| 8 | SERIES | Jul-Aug 2002 | 50.14° N, 144.75° W<br>North Pacific-<br>Eastern subarctic Pacific | RV *John P. Tully*<br>RV *El Puma*<br>RV *Kaiyo Maru* | ①315 (0)<br>②315 (6) | <0.10 | 2.00<br>0.60 | $SF_6$ | 77 | 25 | HNLC |

To be continued

| - | Experiment | Time | Location | Research Vessel | Fe (kg) (day) | Initial Fe (nM) | After Fe (nM) | Tracer | Patch size ($km^2$) | Period (days) | Region |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | EIFEX | Feb–Mar 2004 | 50° S, 2° E<br>Southern Ocean–<br>Atlantic sector | RV *Polarstern* | ①1406 (0)<br>②1406 (13) | 0.20 | 1.50<br>0.34 | | 167 | 39 | HNLC |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | FeeP | Apr–May 2004 | 27.5° N 22.5° W<br>North Atlantic-<br>Subtropical north-east Atlantic | RV *Charles Darwin*<br>RV *Poseidon* | ①1840 (0) | 0.20 | 3.00 | $SF_6$ | 25 | 21 | LNLC |
| 11 | SAGE | Mar–Apr 2004 | 46.7° S 172.5° E<br>Southern Ocean–<br>Southeast of New Zealand | RV *Tangaroa* | ①265 (0)<br>②265 (6)<br>③265 (9)<br>④265 (12) | 0.09 | 3.03<br>1.59<br>0.55<br>1.01 | $SF_6$ | 36 | 15 | HNLCLSi |
| 12 | SEEDS-2 | Jul–Aug 2004 | 48° N, 166° E<br>North Pacific–<br>Western subarctic gyre | RV *Hakuho-Maru*<br>RV *Kilo Moana* | ①332 (0)<br>②159 (6) | 0.17 | 1.38 | $SF_6$ | 64 | 26 | HNLC |
| 13 | LOHAFEX | Jan–Mar 2009 | 48° S, 15° W<br>Southern Ocean– | RV *Polarstern* | ①2000 (0)<br>②2000 (21) | - | 2.00 | $SF_6$ | 300 | 40 | HNLCLSi |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Atlantic sector | | | | | | | | |
| 1 | CROZEX* | Nov 2004 – Jan 2005 | 44° S, 50° E<br>Southern Ocean-South of sub-Antarctic Front | RV *Discovery* | - | 0.04 | 0.55 | - | - | - | HNLC |
| 2 | KEOPS* | Jan–Feb 2005 | 50° S, 73° E<br>Southern Ocean – South of Polar Front | RV *Marion Dufresne* | - | - | - | - | - | - | HNLC |

* Natural OIF experiments

Sources are as follows: Martin et al., 1994; Coale et al., 1996; Coale et al., 1998; Boyd et al., 2000; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004; Bakker et al., 2005; Boyd et al., 2005; Coale et al., 2004; de Baar et al., 2005; Hiscock and Millero, 2005; Nishioka et al., 2005; Tsuda et al., 2005; Tsumune et al., 2005; Boyd et al., 2007; Rees et al., 2007; Tsuda et al., 2007; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012; Martin et al., 2013.

**Table 2.** Summary of OIF experiments; objective, significant results, and limitation

| - | Experiment | Objective | Significant results | Limitation |
|---|---|---|---|---|
| 1 | IronEx-1 | * To test the iron hypothesis | * Increased phytoplankton production in response to added iron | * Relatively small increase in primary production<br>* Rapid loss of iron within mixed layer |
| 2 | IronEx-2 | * To test four hypotheses which were raised by lack of biogeochemical response upon iron addition during IronEx-1 | * A massive phytoplankton bloom response to iron addition<br>* Significant drawdown of $pCO_2$<br>* Diatom-dominated community | * Limited information on export flux<br>* No observation of the fate of the bloom |
| 3 | SOIREE | * To confirm of iron limitation in phytoplankton growth in the Southern Ocean<br>* To understand downward fluxes | * Iron-induced decreases in $pCO_2$<br>* Diatom-dominated bloom with low mesozooplankton grazing | * No increase in export flux<br>* Unknown remineralization |
| 4 | EisenEx | * To artificially stimulate an airborne ‘dust’ episode in the Southern Ocean with OIF | * Maintenance of iron-induced phytoplankton bloom in austral spring | * No difference in POC flux between inside patch and outside patch in the eddy |

| | | | | |
|---|---|---|---|---|
| | | * To study the response of phytoplankton bloom under limited light condition | | |
| 5 | SEEDS-1 | * To test the iron hypothesis in the subarctic North Pacific Ocean<br>* To examine the changes in the species composition and the specific growth responses of key diatom species | * Significant drawdown in $pCO_2$<br>* Shifting from oceanic diatoms to neritic centric diatom | * No increase in export flux<br>* Unknown trophic interactions |
| 6 | SOFeX-N | * To investigate the effects of iron enrichment in regions with low silicate concentrations | * Enhanced growth of diatom groups<br>* $pCO_2$ depressed by increased primary production | * Entrainment of dissolved silicate into the patch by physical mixing |
| 7 | SOFeX-S | * To investigate the effects of iron enrichment in regions with high silicate concentrations | *Increased POC flux out of the mixed layer | *Small POC flux relative to natural blooms |
| 8 | SERIES | * To detect the decline and fate of an iron-fertilized diatom bloom<br>* To measure the response of trophic interactions to iron addition | * Decline and fate of iron-added bloom<br>* Bacterial remineralization and mesozooplankton grazing accounting as main process of POC decrease | * Inefficient transfer of iron-increased POC below the permanent thermocline |

| | | * To measure carbon flux out of the surface layer | | |
|---|---|---|---|---|

To be continued

| - | Experiment | Objective | Significant results | Limitation |
|---|---|---|---|---|
| 9 | EIFEX | * To find out the growth and demise phase of phytoplankton bloom in fertilized patch<br><br>* To confirm the second condition of the iron hypothesis | * Significant enhancement of deep carbon export (>3000 m)<br><br>* The occurrence of rapidly sinking large aggregate | |
| 10 | FeeP | * To understand phosphate and iron limitation in biological activity | *Increased *Trichodesmium* | * No overall shift in phytoplankton community |
| 11 | SAGE | * To understand gas transfer processes and influence of OIF on biologically driven gas exchange | *Successful measurement of gas exchange at strong wind speeds | * No phytoplankton bloom<br><br>* Increase in $pCO_2$ due to physical mixing |

| | | | | |
|---|---|---|---|---|
| 12 | SEEDS-2 | * To determine the fate of an iron-stimulated diatom bloom<br>* To verify the vertical export carbon flux | * Higher abundance of mesozooplankton (copepod) during bloom-development phase | * No extensive diatom bloom |
| 13 | LOHAFEX | * To investigate the fate of iron fertilized bloom biomass related to heterotrophs and export flux under silicate-limiting conditions | * Recycled carbon by grazing and microbial food web in low silicate waters | * Lack of fertilization-induced export due to silicon limitation and bacterial remineralization |

Sources are as follows: Martin et al., 1994; Coale et al., 1996; Coale et al., 1998; Bidigare et al., 1999; Boyd et al., 2000; Charette and Buesseler, 2000; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004; Coale et al., 2004; Bakker et al., 2005; Boyd et al., 2005; de Baar et al., 2005; Hiscock and Millero, 2005; Nishioka et al., 2005; Tsuda et al., 2005; Tsumune et al., 2005; Boyd et al., 2007; Rees et al., 2007; Tsuda et al., 2007; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012; Martin et al., 2013

**Table 3.** Changes of chemical parameters from initial to after concentrations by OIF experiments. Note that *Δ[X] represents changes in concentrations (i.e., $[X]_{post\text{-}fertilization} - [X]_{pre\text{-}fertilization}$).

| | Experiment | Initial $NO_3$ (μM) | *$\Delta NO_3$ (μM) | Initial $PO_4$ (μM) | *$\Delta PO_4$ (μM) | Initial Si (μM) | *ΔSi (μM) | Initial $pCO_2$ (ppm) | *$\Delta pCO_2$ (ppm) | Initial DIC (μM) | *ΔDIC (μM) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | 10.8 | -0.70 | 0.92 | -0.02 | 3.90 | -0.02 | 471 | -13.0 | 2044 | -6.00 |
| 2 | IronEx-2 | 10.4 | -4.00 | 0.80 | -0.25 | 5.10 | -4.00 | 538 | -73.0 | 2051 | -27.0 |
| 3 | SOIREE | 25.0 | -3.00 | 1.50 | -0.24 | 10.0 | -3.00 | 350 | -(38.0-32.0) | | -(18.0-15.0) |
| 4 | EisenEx | 22.0 | -1.00 | 1.60 | -0.10 | 10.0 | 0 | 360 | -(20-18) | | -(15.0-12.0) |
| 5 | SEEDS-1 | 18.5 | -15.8 | | | 31.8 | -26.8 | 390 | -130 | | -58.0 |
| 6 | SOFeX-N | 21.9 | -1.40 | 1.40 | -0.09 | 2.50 | -1.10 | 367 | -26 | 2109 | -14.0 |
| 7 | SOFeX-S | 26.3 | -3.50 | 1.87 | -0.21 | 62.8 | -4.00 | 365 | -36 | 2176 | -21.0 |
| 8 | SERIES | 10.0-12.0 | -(9.00-7.00) | >1.00 | -0.50 | 14.0-16.0 | -(14.0-12.0) | 350 | -85 | 2030 | -37.0 |
| 9 | EIFEX | 25.0 | -1.50 | 1.80 | -0.30 | 19.0 | -11.0 | 360 | -30 | 2135 | -13.5 |
| 10 | FeeP | <0.01 | | 0.01 | | | | | | | <-1.00 |
| 11 | SAGE | 7.90-10.3 | 1.50-3.90 | 0.62-0.85 | | 0.83-0.97 | | 330 | 8.00 | 2057 | 25.0 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ~~12~~ | ~~SEEDS-2~~ | ~~18.4~~ | ~~-5.72~~ | | | ~~36.1~~ | ~~370~~ | ~~-6.00~~ |
| ~~13~~ | ~~LOHAFEX~~ | ~~20.0~~ | ~~-2.50~~ | ~~1.30~~ | ~~-0.20~~ | ~~0.50–1.40~~ | ~~357.5~~ | ~~-(15–7)~~ |

~~Sources are as follow: Martin et al., 1994; Steinberg et al., 1998; Boyd et al., 2000; Bakker et al., 2001; Frew et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Smetacek et al., 2005; Takeda and Tsuda, 2005; Wong et al., 2006; Boyd et al. 2007; Tsumune et al., 2009; Harvey et al., 2010; Smetacek and Naqvi, 2010; Berg et al., 2011; Currie et al., 2011; Law et al., 2011.~~

**Table 4.** Changes of biological parameters from initial to after (maximum) concentrations by OIF experiments. Note that *PP (mg C m$^{-2}$ d$^{-1}$) was estimated by multiplying PP (mg C m$^{-3}$ d$^{-1}$) with mixed layer depth (m).

| - | Experiment | Initial Fv/Fm | Maximum Fv/Fm | Initial Chlorophyll (mg m$^{-3}$) | Maximum Chlorophyll (mg m$^{-3}$) | Initial PP (mg C m$^{-2}$ d$^{-1}$) | Maximum PP (mg C m$^{-2}$ d$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | 0.30 | 0.60 | 0.24 | 0.65 | 300–450* | 805–1330* |
| 2 | IronEx-2 | 0.25 | 0.50 | 0.15–0.20 | 4.00 | 630 | 2430 |
| 3 | SOIREE | 0.22 | 0.65 | 0.25 | 2.00 | 120 | 1300 |
| 4 | EisenEx | 0.30 | 0.56 | 0.50 | 2.50 | 130–220 | 790 |
| 5 | SEEDS-1 | 0.19 | 0.31 | 0.80–0.90 | 21.8 | 420 | 1670 |
| 6 | SOFeX-N | 0.20 | 0.5 | 0.15 | 2.60 | 144 | 1500 |
| 7 | SOFeX-S | 0.25 | 0.65 | 0.30 | 3.80 | 216 | 972 |
| 8 | SERIES | 0.24 | 0.55 | 0.35 | 5.00 | 300 | 2000 |
| 9 | EIFEX | 0.28 | 0.6 | 0.70 | 3.16 | 750 | 1500 |
| 10 | FeeP | - | - | 0.04 | 0.07 | - | - |
| 11 | SAGE | 0.27 | 0.61 | 0.63 | 1.33 | 540 | 900 |
| 12 | SEEDS-2 | 0.29 | 0.40 | 0.80 | 2.48 | 390 | 1000 |
| 13 | LOHAFEX | 0.33 | 0.40–0.50 | 0.50 | 1.25 | 960 | 1560 |

Sources are as follow: Kolber et al., 1994; Martin et al., 1994; Behrenfeld et al., 1996; Steinberg et al., 1998; Boyd et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; de Baar et al., 2005; Takeda and Tsuda, 2005;

~~Tsuda et al., 2005; Assmy et al., 2007; Boyd et al., 2007; Tsuda et al., 2007; Kudo et al., 2009; Harvey et al., 2010; Berg et al., 2011; Currie et al., 2011; Peloquin et al., 2011; Smetacek et al., 2012; Thiele et al., 2012; Martin et al., 2013; Latasa et al., 2014.~~

**Table 5**. Export flux (mg C m$^{-2}$ d$^{-1}$); initial and maximum values in patch at each depth (measurement day from the beginning of OIF experiment), initial and maximum values outside patch at each depth (measurement day from the beginning of OIF experiment), measurement depth, measurement method, and method description to detect enhanced export production.

| | Experiment | In patch Initial (day) | In patch Maximum (day) | Outside Initial (day) | Outside Maximum (day) | Depth (m) | Method | Method description |
|---|---|---|---|---|---|---|---|---|
| 1 | IronEx-1 | | | | | | | |
| 2 | IronEx-2 | 84 (0) | 600 (7) | | | 25 | $^{234}Th$ | *Water column at 0, 25 m ($^{234}Th$, $^{13}C_{org}$) |
| | | | | | | | | *Water column in the upper 100 m ($^{234}Th$, $^{13}C_{org}$) |
| 3 | SOIREE | 146/73 (0) | 193/74 (11) | 146/73 (0) | 78/38 (11) | 110/310 | $^{234}Th$, trap | *Free-drifting sediment traps at 110, 310 m ($^{234}Th$, $^{13}C_{org}$, total mass, POC, biogenic silica (BSi), particulate organic nitrogen (PON)) |
| | | | | | | | | *Transmissometer |
| | | | | | | | | *Water column ($^{234}Th$) |
| 4 | EisenEx | | | | | | | *Sediment trap at 20, 500, 3500 m (POC) |
| 5 | SEEDS-1 | 374/166 (2) | 1000/140 (13) | | | 50/200 | $^{234}Th$, trap | *Water column in the upper 200 m (POC, PON, BSi, $^{234}Th$) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | *Drifting sediment trap at 40, 60, 100, 200 m (POC, PON, BSi, $^{234}Th$) |
| 6 | SOFeX-N | | | | | | | *Autonomous floats profiling transmissometer<br>*Water column ($^{234}Th$, POC) |
| 7 | SOFeX-S | 36/19 (6) | 112/142 (27) | 48/38 (7) | 49/56 (27) | 50/100 | $^{234}Th$ | *Water column at 25, 50, 75, 100, 125 m ($^{234}Th$, POC, PON, BSi)<br>*Water column in the upper 110 m (POC, BSi) |
| 8 | SERIES | 120/48 (3) | 480/192 (24) | 192 (3) | 139 (15) | 50/100 | $^{234}Th$, trap | *Free-drifting sediment traps at 100 and 300 m (POC, BSi, $^{234}Th$)<br>*Transmissometer |
| 9 | EIFEX | 340 (0) | 1692 (32) | 396 (0) | 516 (32) | 100 | $^{234}Th$ | *Sediment trap in the 1000 m upper layer (BSi, POC, PON, $^{234}Th$, $^{13}C_{org}$, PON, stable nitrogen isotope of PON ($^{15}N_{PON}$)) |
| 10 | FeeP | | | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11 | SAGE | | | | | | | *Free-drifting sediment traps at 80, 300 m (POC, PON, BSi)<br>*Particle camera deployments |
| 12 | SEEDS-2 | 290/316<br>(1-4) | 580/336<br>(19-22) | 299/212<br>(1-8) | 509/204<br>(18-31) | 40/100 | Trap | *Water column in the upper 100 m (POC, PON, BSi, $^{13}C_{org}$)<br>*Drifting sediment trap at 40, 70, 100 m (POC, PON, BSi, $^{13}C_{org}$) |
| 13 | LOHAFEX | 60 (0) | 94 (23) | 78 (4) | 97 (25) | 100 | $^{234}$Th | *Neutrally buoyant sediment traps at 200, 450 m (POC, PON, $^{234}$Th)<br>*Underwater video profiler<br>*Water column in the upper 100 m (POC, PON, $^{234}$Th) |

Sources are as follow: Bidigare et al., 1999; Nodder et al., 2001; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001; Bishop et al., 2004; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Jacquet et al., 2008; Aramaki et al., 2009; Berg et al., 2011; Peloquin et al., 2011; Smetacek et al., 2012; Martin et al., 2013.

**Figure Captions**

**Fig. 1.** Diagram showing the monthly atmospheric $CO_2$ concentrations (ppm) (blue) according to the Mauna Loa Observatory, Hawaii (http://www.esrl.noaa.gov/gmd/ccgg/trends/data.html), global monthly land surface air and sea surface temperature anomalies (°C) (red) (http://data.giss.nasa.gov/gistemp/), and pH (green) measured at station ALOHA in the central Pacific (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt). The data values represent moving average values for 12 months and shading indicates the standard deviation of 12 months.

**Fig. 2.** Schematic representation of several proposed climate-engineering methods (modified from Matthews, 1996).

**Fig. 3.** The iron hypothesis as suggested by Martin (1990). (a) Efficiency of the biological pump under normal conditions and (b) efficiency of the biological pump as a result of Fe enrichment. DIC is dissolved inorganic carbon and OM is organic matter (modified from Sarmiento and Gruber, 2006).

**Fig. 4.** Global annual distribution of surface (a) chlorophyll concentrations (mg $m^{-3}$), (b) nitrate concentrations (μM), and (c) silicate concentrations (μM). Chlorophyll-a concentration distribution represents the Aqua MODIS chlorophyll-a composite from July 2002 to February 2016 (http://oceancolor.gsfc.nasa.gov/cgi/l3), while the nitrate and silicate were plotted by Ocean Data View program (https://odv.awi.de) using the World Ocean Atlas 2013 dataset (https://odv.awi.de/en/data/ocean/world_ocean_atlas_2013). White circles indicate the locations of 13 artificial OIF experiments and black triangles indicate the locations of natural OIF experiments. Note that the numbers indicate the order of experiments (see Table 1).

**Fig. 5.** Photographs of iron the addition procedure. Panels a-e taken during EIFEX and LOHAFEX: (a) Iron (II) sulfate bags, (b) the funnel where iron and hydrochloric acid were poured, (c) tank system for mixing with Iron(II) sulfate, hydrochloric acid, and seawater, (d) outlet pipe connected with tank system, (e) pumping iron into prop wash during EIFEX (Smetacek, 2015).

**Fig. 6.** (a) Patch size ($km^2$) for first Fe addition (blue bar) and maximum patch size (sky blue bar) during OIF experiments. (b) Amounts (kg) of first Fe addition (blue bar) and total Fe addition (sky blue bar). (c) Minimum (blue bar) and maximum (sky blue bar) mixed layer depth (m). (d) Average sea surface temperature (°C). Initial (e) nitrate concentrations (μM), (f) silicate concentrations (μM), (g) Fv/Fm ratio, and (h) chlorophyll-a concentrations (mg $m^{-3}$) before iron addition. Note that the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Harvey et al., (2010); Berg et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

**Fig. 7.** (a) Initial (coral bar) and maximum (light coral bar) Fv/Fm ratio during OIF experiments. (b) Changes in nitrate concentrations ($\Delta$Nitrate = $[NO_3^-]_{post-fertilization}$ – $[NO_3^-]_{pre-fertilization}$; μM). (c) Initial (coral bar) and maximum (light coral bar) chlorophyll-a concentrations (mg $m^{-3}$). (d) Distributions of chlorophyll-a concentrations (mg $m^{-3}$) at ~28 days after iron addition in the SOFeX-N and at ~20 days in the SOFeX-S. White dotted box indicates phytoplankton bloom during OIF

experiments. Changes in (e) primary productivity ($\Delta PP = [PP]_{post\text{-}fertilization} - [PP]_{pre\text{-}fertilization}$; mg C $m^{-2}$ $d^{-1}$) and in (f) $pCO_2$ ($\Delta pCO_2 = [pCO_2]_{post\text{-}fertilization} - [pCO_2]_{pre\text{-}fertilization}$; ppm). Color bar indicates changes in DIC ($\Delta DIC = [DIC]_{post\text{-}fertilization} - [DIC]_{pre\text{-}fertilization}$; μM). Note that PP (mg C $m^{-2}$ $d^{-1}$) of OIF experiment number 1 (IronEx-1) was estimated by multiplying PP (mg C $m^{-3}$ $d^{-1}$) with mixed layer depth and the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Bakker et al., (2001); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Bakker et al., (2005); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Smetacek et al., (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Wong et al., (2006); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Kudo et al., (2009); Tsumune et al., (2009); Harvey et al., (2010); Smetacek and Naqvi, (2010); Berg et al., (2011); Currie et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

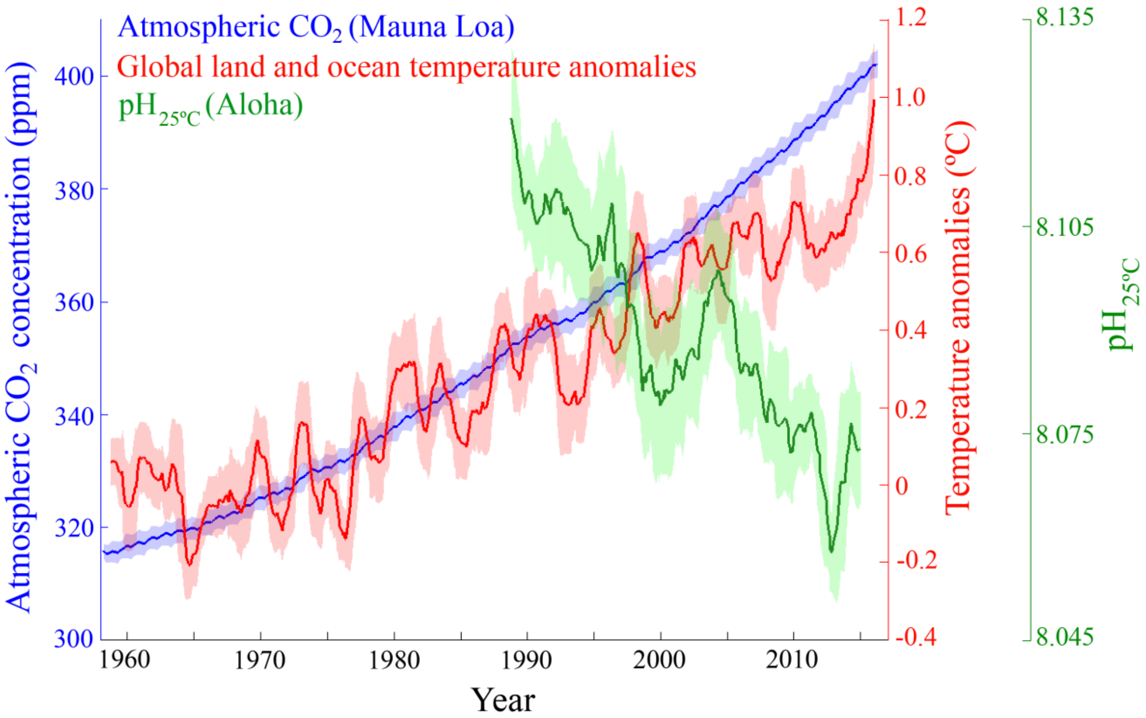
**Fig. 8.** Time-series of (a) $^{234}$Th-derived particulate organic carbon (POC) fluxes (mg $m^{-2}$ $d^{-1}$) of the upper 100 m layer in patch (coral bar) and outside patch (blue bar) during EIFEX (modified from Smetacek et al., 2012). Time-series of (b) vertically integrated $^{234}$Th (dpm $l^{-1}$) in patch (coral circle) and outside patch (blue diamond) relative to parent $^{238}$U (dpm $l^{-1}$; dotted black line) during SOIREE (modified from Nodder et al., 2001).

**Fig. 9.** Assessment framework for scientific research involving ocean fertilization (OF) (modified from Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).

**Fig. 10.** (a) Time-series of mixed layer depth-integrated chlorophyll-a concentrations (mg $m^{-2}$) during SOIREE (pink line), SEEDS-1 (brown line), SERIES (cyan line), SEEDS-2 (blue line), and EIFEX (teal line). Sources are as follows: Boyd and Abraham, (2001); Tsuda et al., (2007); Assmy et al., (2013). (b) The distributions of chlorophyll-a concentrations (mg $m^{-3}$) in ~5 days and ~46 days during SOIREE from SeaWiFS Level-2 daily images.

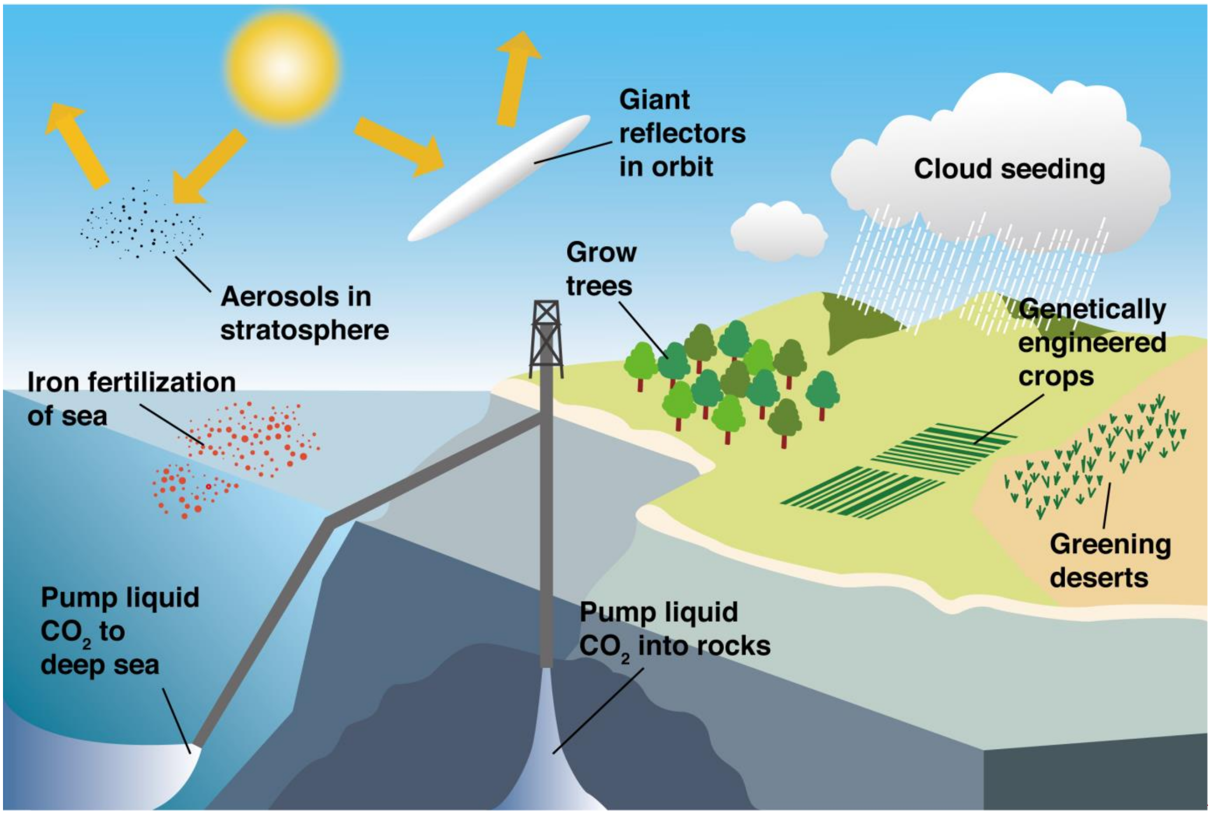
**Fig. 11.** Schematic diagram of KIFES representing experiment target site (eddy structure) and survey methods (underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations).

~~**Fig. 1**~~

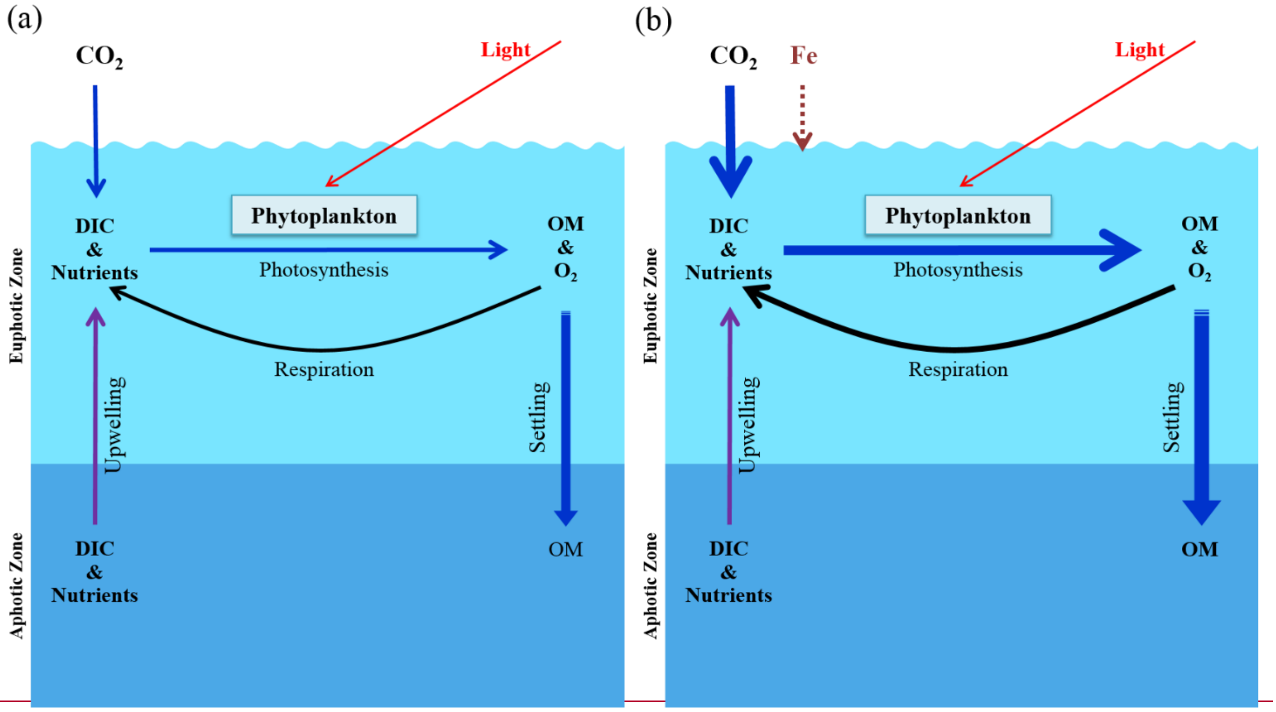


Atmospheric CO2 (Mauna Loa)
Global land and ocean temperature anomalies
pH25ºC (Aloha)
Atmospheric CO2 concentration (ppm)
Temperature anomalies (ºC)
pH25ºC
Year

~~Fig. 2~~

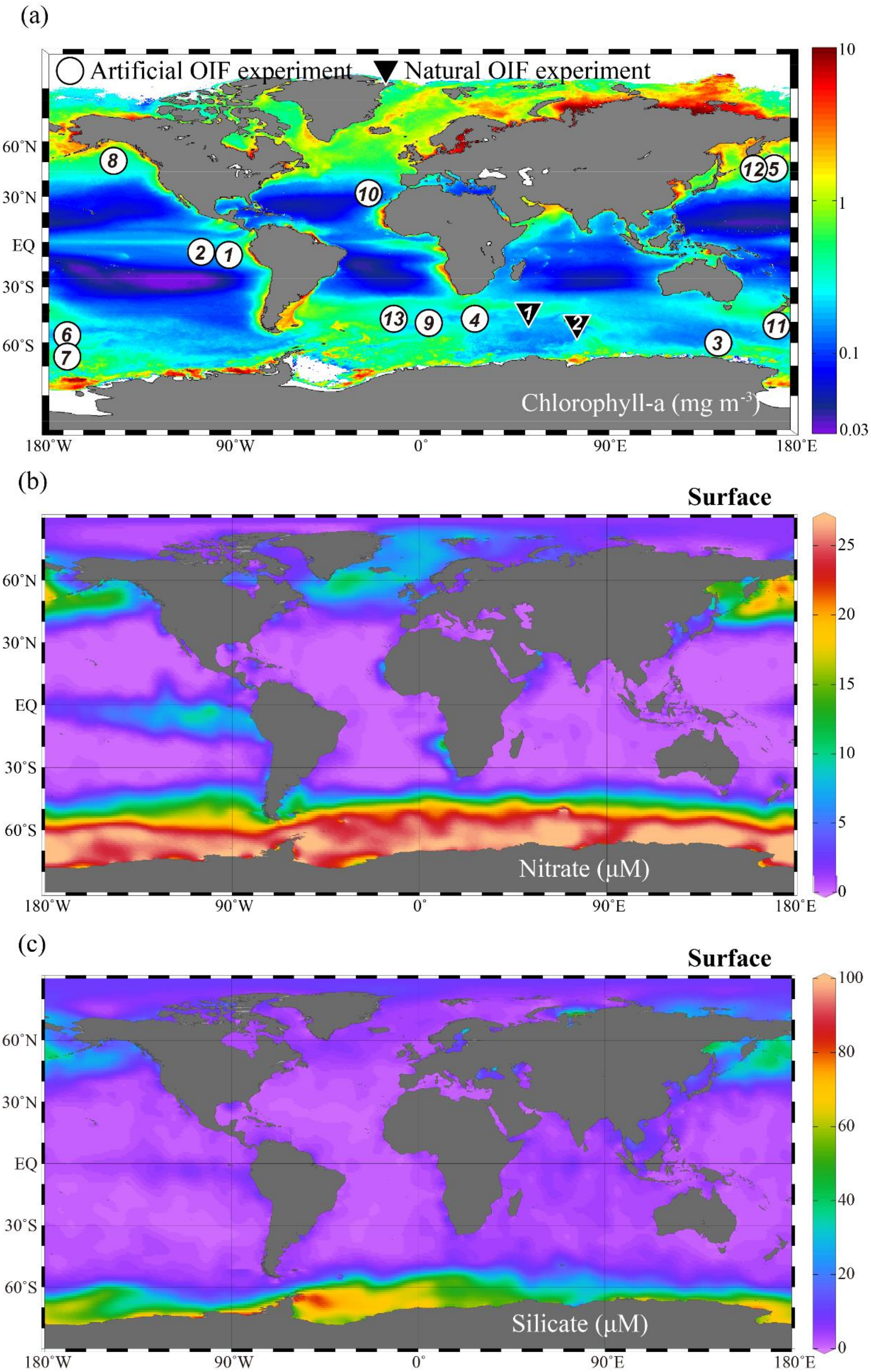

Giant
reflectors
in orbit
Cloud seeding
Aerosols in
stratosphere
Grow
trees
Genetically
engineered
crops
Iron fertilization
of sea
Greening
deserts
Pump liquid
$CO_2$ to
deep sea
Pump liquid
$CO_2$ into rocks

~~Fig. 3~~



(a)
$CO_2$
Light
Phytoplankton
DIC & Nutrients
Photosynthesis
OM & $O_2$
Respiration
Euphotic Zone
Upwelling
Settling
Aphotic Zone
DIC & Nutrients
OM
(b)
$CO_2$
Fe
Light
Phytoplankton
DIC & Nutrients
Photosynthesis
OM & $O_2$
Respiration
Euphotic Zone
Upwelling
Settling
Aphotic Zone
DIC & Nutrients
OM

~~Fig. 4~~



(a)
Artificial OIF experiment
Natural OIF experiment
Chlorophyll-a (mg m-3)
10
1
0.1
0.03
60°N
30°N
EQ
30°S
60°S
180°W
90°W
0°
90°E
180°E
(b)
Surface
Nitrate (μM)
25
20
15
10
5
0
(c)
Surface
Silicate (μM)
100
80
60
40
20
0

~~**Fig. 5**~~

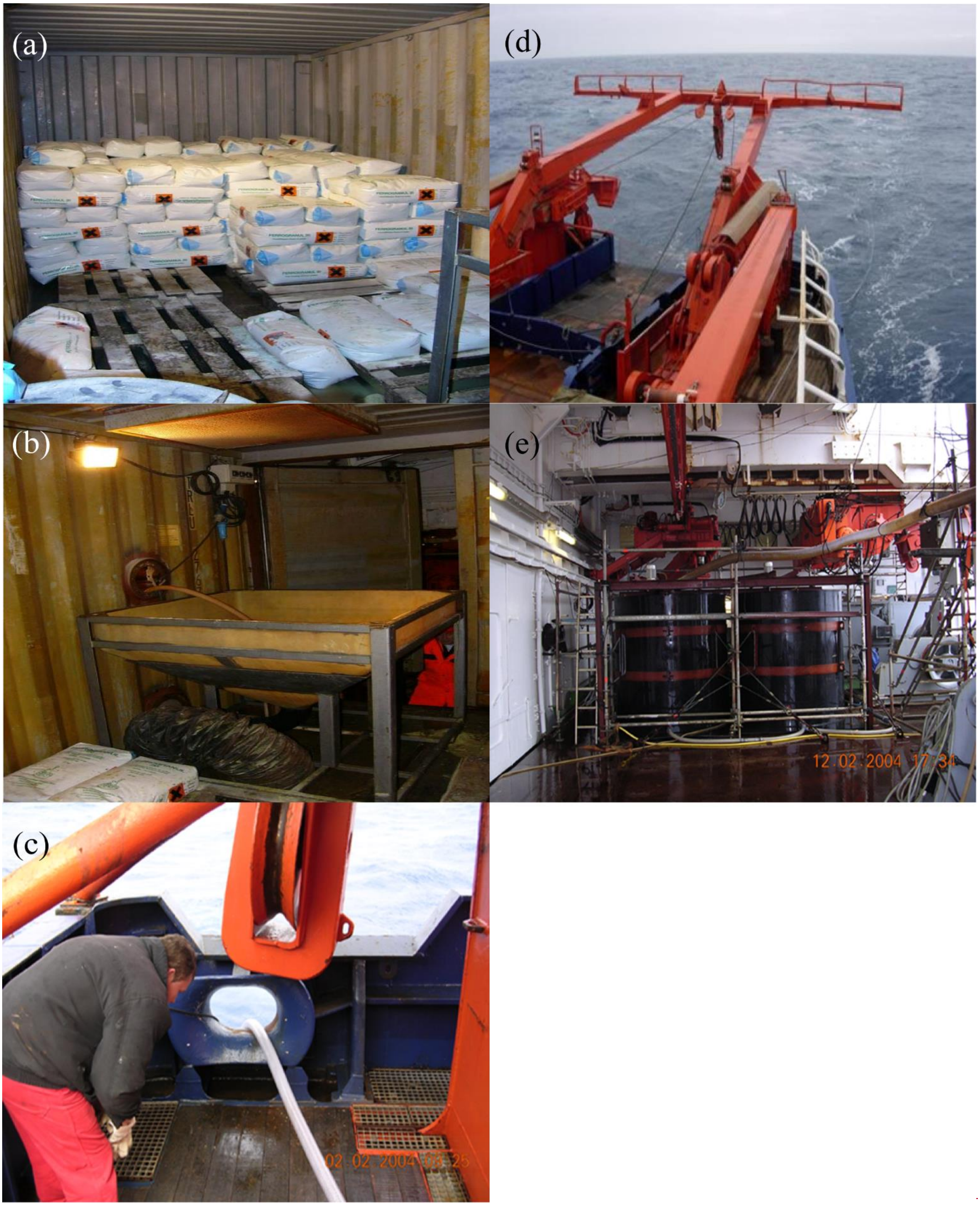
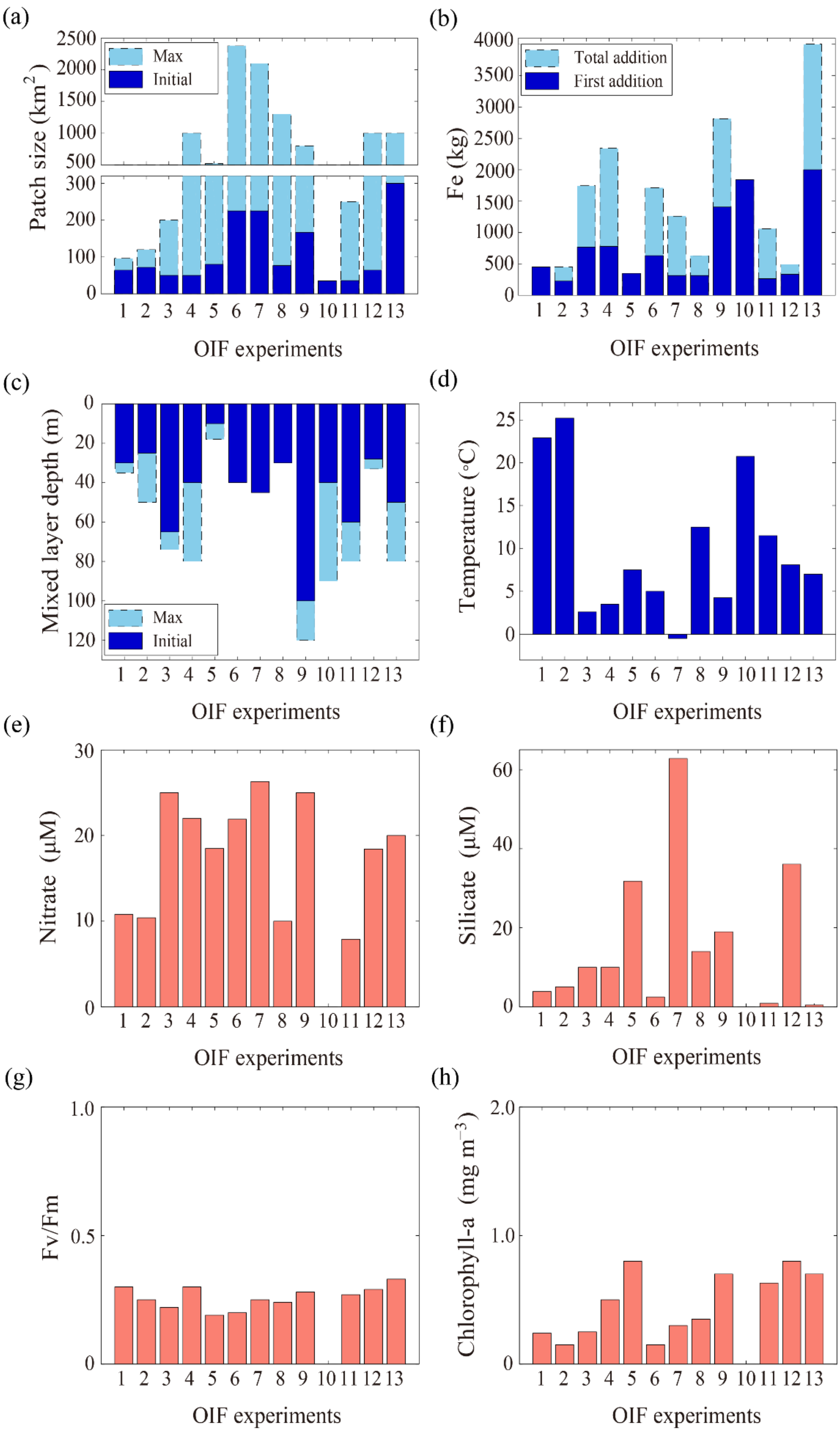
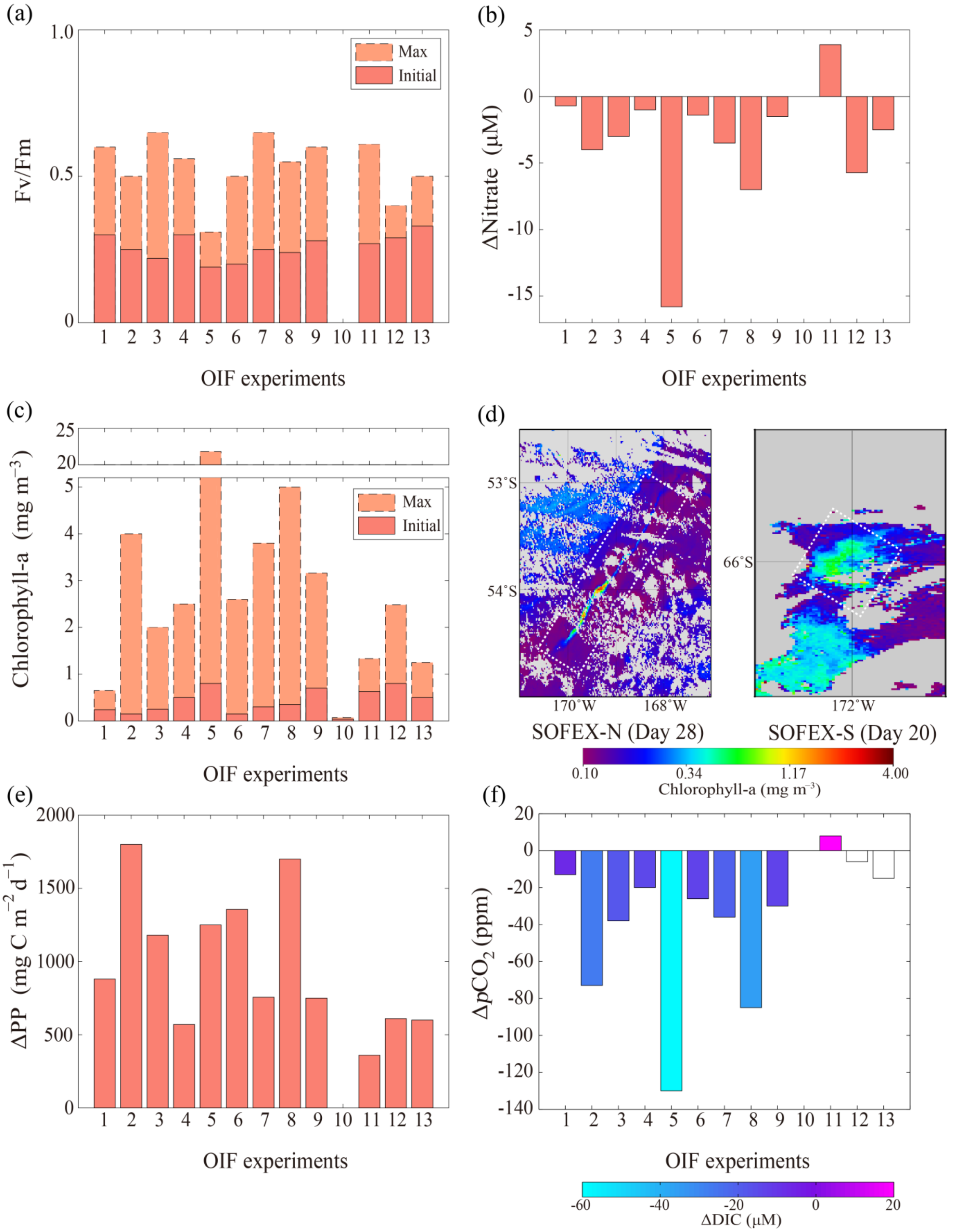


Fig. 6

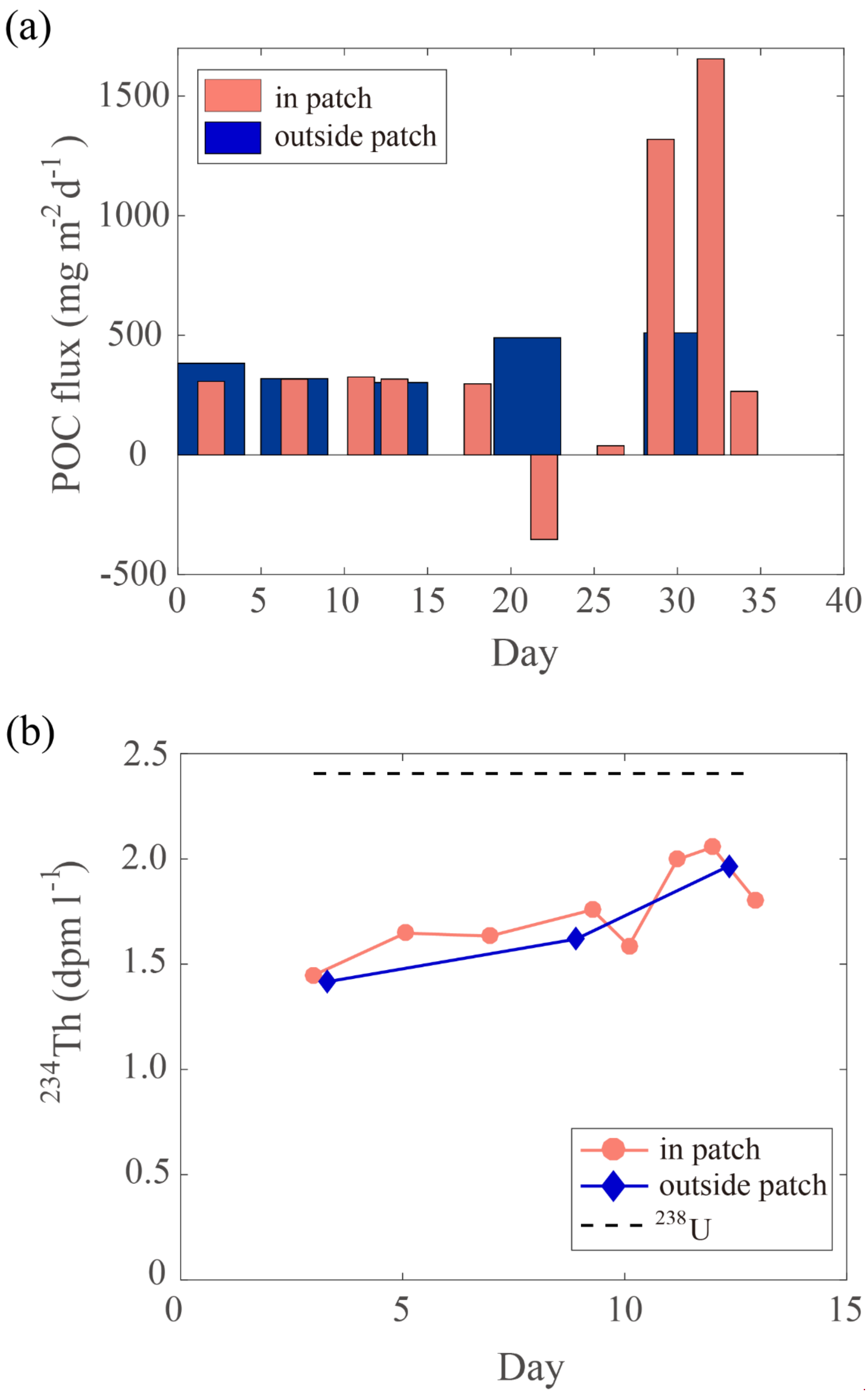

(a)
Patch size (km$^2$)
Max
Initial
OIF experiments
(b)
Fe (kg)
Total addition
First addition
OIF experiments
(c)
Mixed layer depth (m)
Max
Initial
OIF experiments
(d)
Temperature (°C)
OIF experiments
(e)
Nitrate (μM)
OIF experiments
(f)
Silicate (μM)
OIF experiments
(g)
Fv/Fm
OIF experiments
(h)
Chlorophyll-a (mg m$^{-3}$)
OIF experiments

~~Fig. 7~~

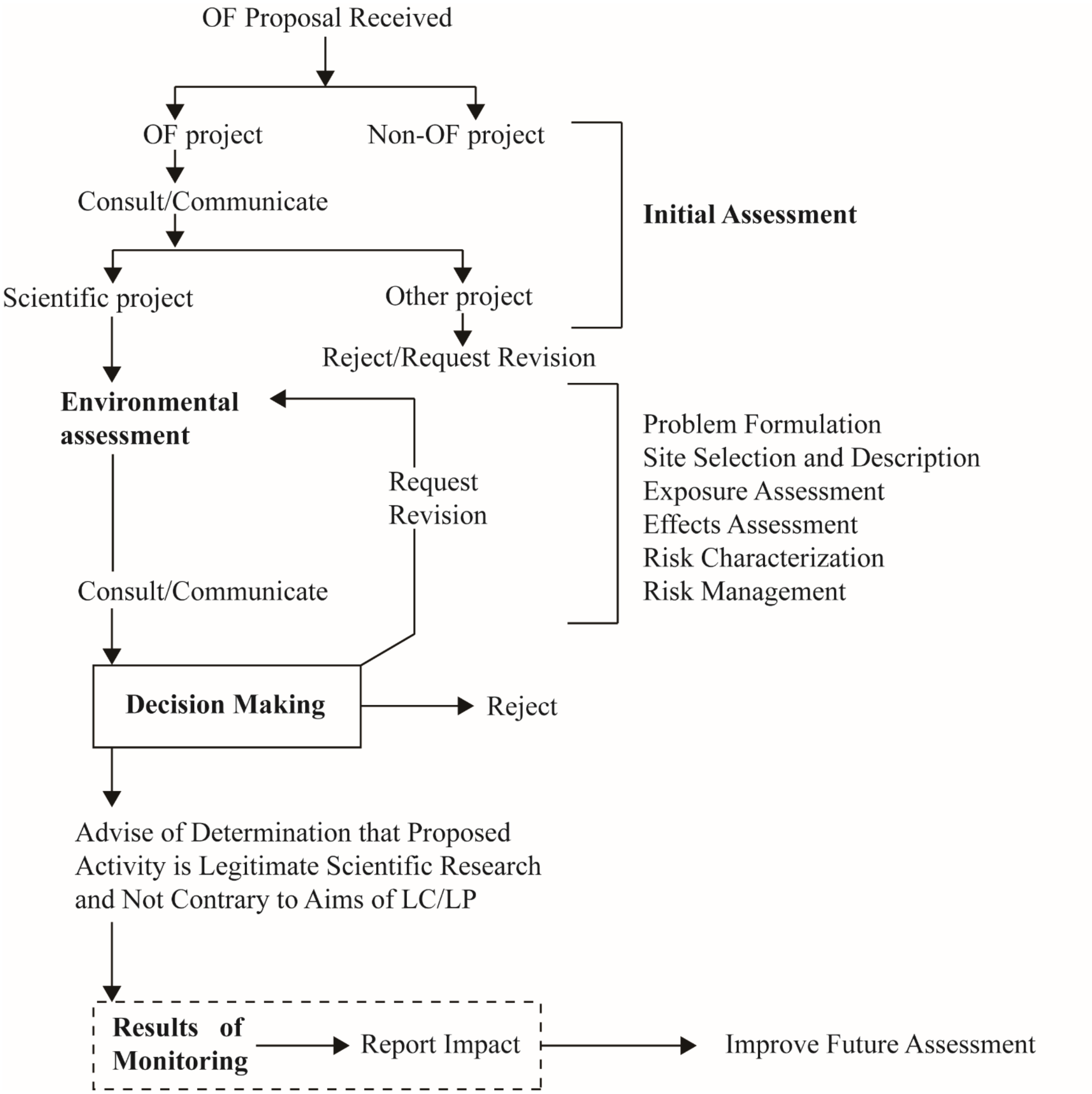


(a)
Fv/Fm
1.0
0.5
0
Max
Initial
1 2 3 4 5 6 7 8 9 10 11 12 13
OIF experiments
(b)
ΔNitrate (μM)
5
0
-5
-10
-15
1 2 3 4 5 6 7 8 9 10 11 12 13
OIF experiments
(c)
Chlorophyll-a (mg m$^{-3}$)
25
20
5
4
3
2
1
0
Max
Initial
1 2 3 4 5 6 7 8 9 10 11 12 13
OIF experiments
(d)
53°S
54°S
170°W
168°W
66°S
172°W
SOFEX-N (Day 28)
SOFEX-S (Day 20)
0.10
0.34
1.17
4.00
Chlorophyll-a (mg m$^{-3}$)
(e)
ΔPP (mg C m$^{-2}$ d$^{-1}$)
2000
1500
1000
500
0
1 2 3 4 5 6 7 8 9 10 11 12 13
OIF experiments
(f)
Δ$p$CO$_2$ (ppm)
20
0
-20
-40
-60
-80
-100
-120
-140
1 2 3 4 5 6 7 8 9 10 11 12 13
OIF experiments
-60
-40
-20
0
20
ΔDIC (μM)

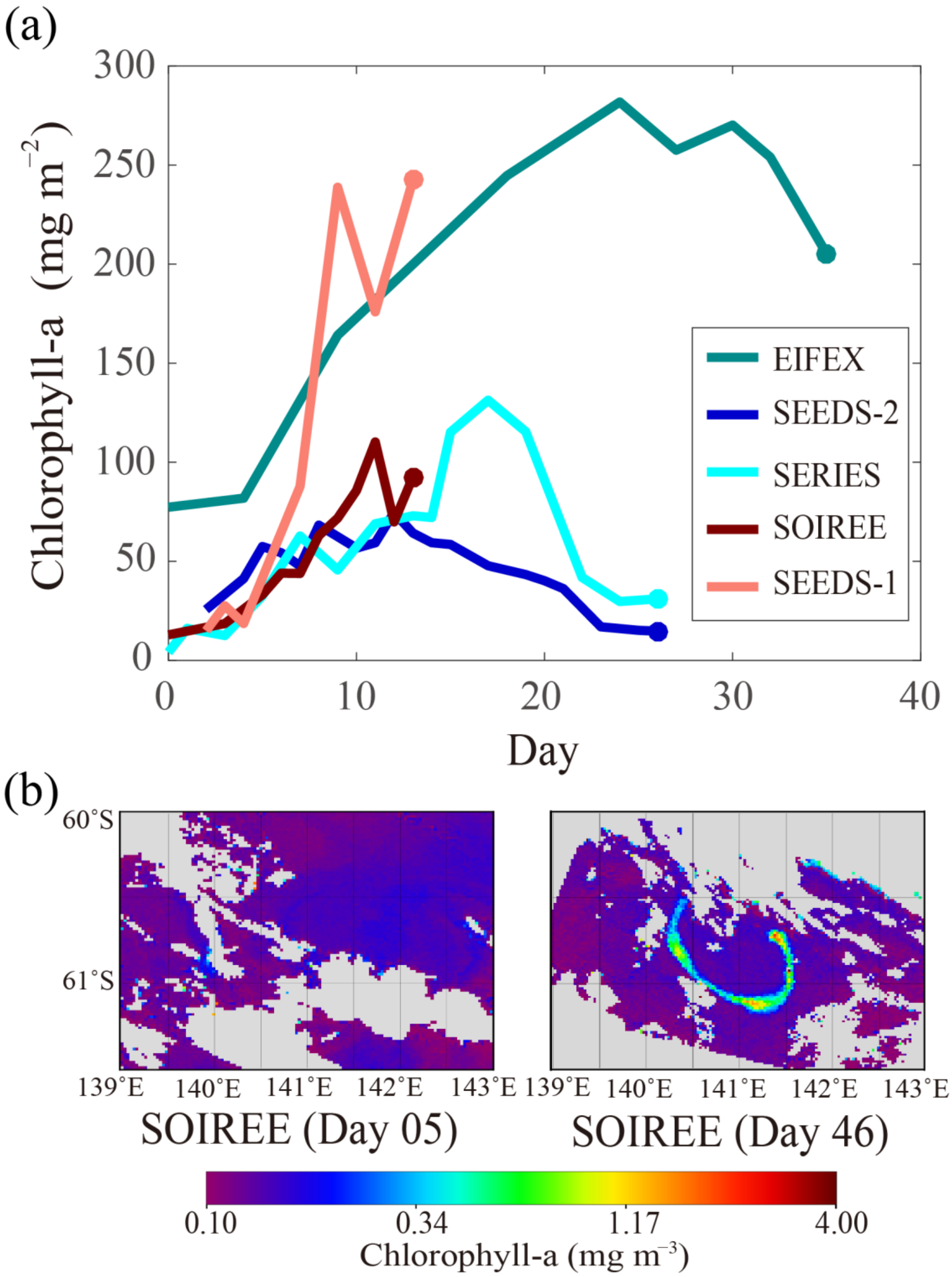
Fig. 8


(a)
in patch
outside patch
POC flux (mg m-2 d-1 )
1500
1000
500
0
-500
0 5 10 15 20 25 30 35 40
Day
(b)
2.5
2.0
1.5
1.0
0.5
0
234Th (dpm l-1)
in patch
outside patch
238U
0 5 10 15
Day

~~Fig. 9~~

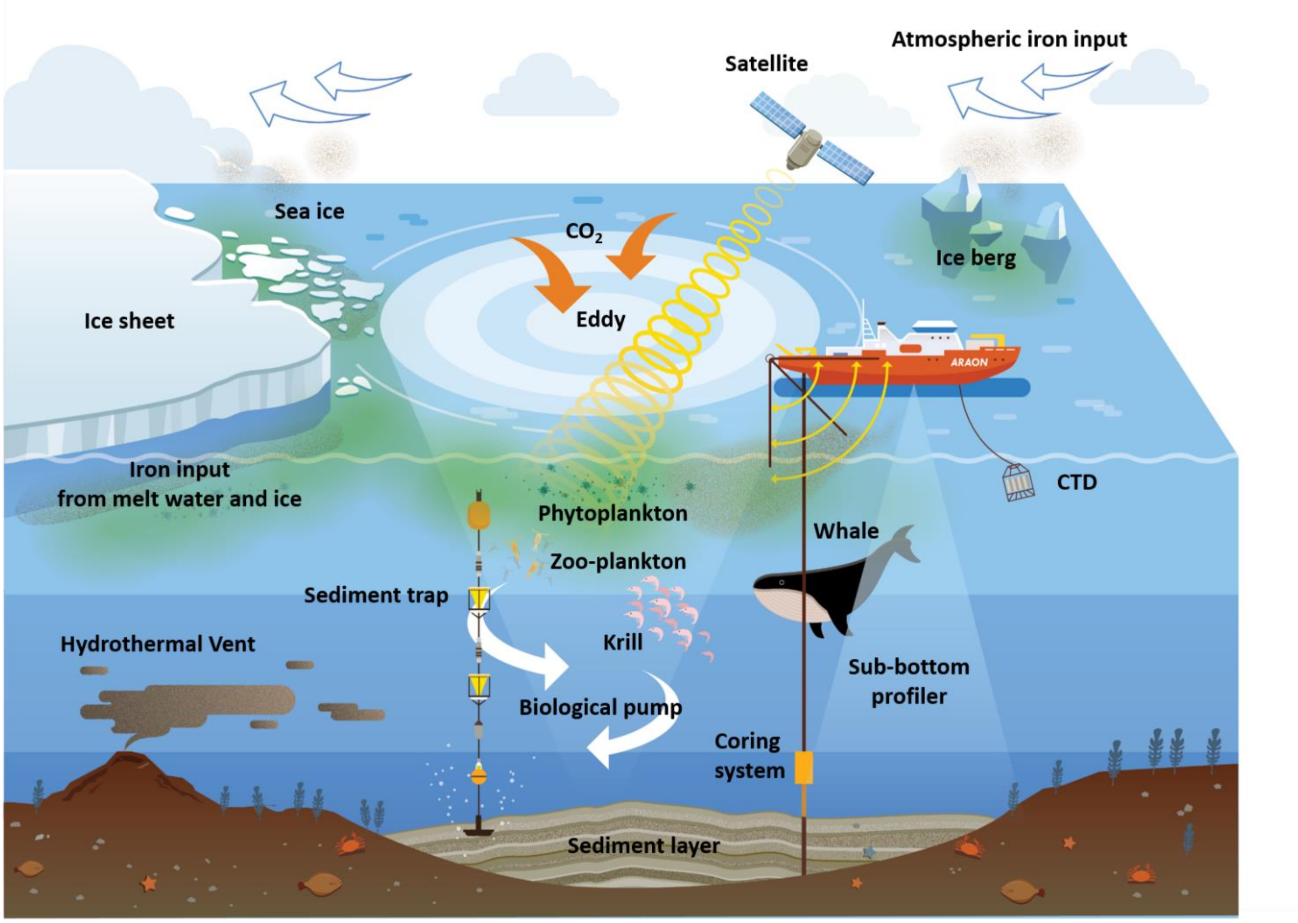

OF Proposal Received
OF project
Non-OF project
Consult/Communicate
Initial Assessment
Scientific project
Other project
Reject/Request Revision
Environmental assessment
Problem Formulation
Site Selection and Description
Exposure Assessment
Effects Assessment
Risk Characterization
Risk Management
Request Revision
Consult/Communicate
Decision Making
Reject
Advise of Determination that Proposed Activity is Legitimate Scientific Research and Not Contrary to Aims of LC/LP
Results of Monitoring
Report Impact
Improve Future Assessment

~~**Fig. 10**~~



(a)
Chlorophyll-a (mg m$^{-2}$)
300
250
200
150
100
50
0
0
10
20
30
40
Day
EIFEX
SEEDS-2
SERIES
SOIREE
SEEDS-1
(b)
60°S
61°S
139°E
140°E
141°E
142°E
143°E
SOIREE (Day 05)
SOIREE (Day 46)
0.10
0.34
1.17
4.00
Chlorophyll-a (mg m$^{-3}$)

~~Fig. 11~~



Atmospheric iron input
Satellite
Sea ice
$CO_2$
Ice berg
Ice sheet
Eddy
ARAON
Iron input
from melt water and ice
CTD
Phytoplankton
Whale
Zoo-plankton
Sediment trap
Krill
Hydrothermal Vent
Sub-bottom
profiler
Biological pump
Coring
system
Sediment layer