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Ocean Iron Fertilization Experiments: Past–Present–Future with Introduction to Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) Project

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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 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, export production efficiency 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 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 considerations including possible side effects (present), and an introduction to the OIF experiment plan currently being designed by Korean oceanographers (future).

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, 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, 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). High export production/carbon sequestration efficiencies 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 (3) to introduce the plans for the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) currently being designed by Korean oceanographers.

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. The unique prior ocean conditions for the various experiments are described in Section 2.2. Tracing the OIF effects is described in Section 2.3 and biogeochemical responses to the OIF experiments are presented in Section 2.4.

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 Chisolm, 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).

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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. 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 2 and 3). 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 2). 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 2 and 3).

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 2). 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 2). Consistent with the World Ocean Circulation Experiment sections and maps (Talley et al., 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 2). 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, the Fv/Fm ratio, a measure of the photosynthetic efficiency of phytoplankton, 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 3) 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 3). 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, 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 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), 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

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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 3 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., ΔNitrate = $[NO_3^-]_{post\text{-}fertilization}$ − $[NO_3^-]_{pre\text{-}fertilization}$ < 0) occurred in all the OIF experiments, except SAGE (Table 2 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 mixed layer depth and lateral advection of high nutrient waters (Table 2 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 3) 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 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). Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images showed that increased chlorophyll-a concentrations after iron addition were appeared at ~28 days after iron addition in the SOFeX-N with a long thread shape (1.0 mg m^{-3}) and at ~20 days in the SOFeX-S over somewhat broad area (0.4 mg m^{-3}) (Fig. 7d) (Westberry et al., 2013).

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).

Associated with the OIF-induced phytoplankton blooms, the magnitude of primary productivity integrated from 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 3). As a result of increased ΔPP, drawdown of pCO_2 (negative ΔpCO_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 ΔpCO_2: sea→air) (Currie et al., 2011). The largest ΔpCO_2 change occurred in SEEDS-1 conducted in the subarctic North Pacific. It also produced the largest ΔNitrate and the greatest chlorophyll increase (Fig. 7f) (Tsuda et al., 2003; de Baar et al., 2005). Overall, OIF ΔpCO_2 reductions ranged from -6 ppm (SEEDS-2) to -130 ppm (SEEDS-1) (Table 2 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).

Early OIF experiments showed that iron addition stimulates the first step of biological pump, promotion of phytoplankton growth. To determine whether the second step of biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, sediment trap and chemical tracers such as natural radiotracer thorium-234 (^{234}Th; half-life = 24.1 days) have been used together and/or individually to estimate the export flux of particulate organic carbon (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). ^{234}Th 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). During IronEx-2, ^{234}Th deficiency was evident in the iron fertilized patch indicating iron-stimulated export production, however there were no ^{234}Th observations conducted in as unfertilized patch for comparison (Bidigare et al., 1999) (Fig. 8b). During EIFEX, initial export flux estimated using ^{234}Th in the upper 100 m of the fertilized patch was 340 mg C m^{-2} d^{-1}. This value remained constant for 25 days after iron addition (Fig. 8a). Then, between 30 and 36 days after iron addition, a massive increase of 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 (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 effect of iron addition on this component of the biological pump remains a question that needs to be resolved possibly by future OIF experimentation (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).

3 Present: OIF debates and considerations

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). On the other hand, the ocean is already a significant source for atmospheric N_2O, so 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 in N_2O production was observed in the pycnocline after iron addition (Law and Ling, 2001). This phenomenon was also illustrated in a modeling study of long-term and large-scale OIF (Jin and Gruber, 2003). Complicating the story, however, excess N_2O was not found after iron addition during EIFEX, the second-longest experiment (~39 days) (Walter et al., 2005).

Decomposition of iron addition-enhanced biomass may cause decrease oxygen concentrations in the subsurface waters (Williamson et al., 2012). Box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). 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 be occurred by increased downward carbon exports that elevate microbial respiration (Fuhrman and Capone, 1991).

Dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, was measured during all OIF experiments (Lawrence, 2002). Significant increases in DMS production were found in some of the OIF experiments (i.e., IronEx-2, SOIREE, EisenEx, and SOFeX-N) (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). In particular, DMS production increased 6.5-fold after iron addition during SOIREE (Turner et al., 2004). However, there were no significant changes in DMS production after iron addition during IronEx-1, SEEDS-1, and SEEDS-2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). In the SERIES experiment, DMS production decreased due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production.

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).

The change of phytoplankton community after iron addition discussed in Section 2.4 also has unintended consequences (Silver et al., 2010; Trick et al., 2010). *In situ* measurements and ship-board culture experiments showed that iron enrichment stimulated growth of the toxigenic diatom genus '*Pseudo-nitzschia*', known to produce neurotoxin domoic acid (DA) that has detrimental marine ecosystem impacts (Trick et al., 2010). For example, during IronEx-2 and SOFeX-S, diatoms belonging to the genus '*Pseudo-nitzschia'* dominated the phytoplankton community and high levels of DA were produced (45 ng of DA l^{-1} in IronEx-2 and 220 ng of DA l^{-1} in SOFeX-S; Silver et al., 2010). However, no DA was found during EisenEx, even though generally '*Pseudo-nitzschia'* was the dominant diatom bloom species (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 the conclusion of OIF experimentation as a carbon removal strategy (Boyd et al., 2007). Therefore, evaluation and prediction are paramount. It continues to be a valuable exercise to attempt to answer scientific questions about the efficiency of OIF as a means of reducing atmospheric CO_2 as well as to quantify the possible OIF side effects.

3.2 Designing future OIF experiments: Direction and Considerations

Scientific research on OIF has focused on improving our understanding of the efficiency, 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, 2015). It is therefore of paramount importance that future OIF experiments continue to focus on the efficiency and capacity of OIF as a means of reducing of atmospheric CO_2, but in doing so should carefully consider major factors such as amount/patch size associated with iron addition (i.e., 'How'), location (i.e., 'Where'), and timing (i.e., 'When') to build on the results of OIF experiments as to 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. IronEx-1 is a good example of a successful OIF experiment. The IronEx-1 patch was fertilized with acidified iron(II) sulfate and 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 (Martin et al., 1994). Many subsequent OIF experiments adopted the methods introduced from the 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). This success suggests that there is no need to completely redesign OIF experimentation as the previous designs and methods are a good reference for future efforts.

Where: The second consideration for a successful OIF experiment is the selection of location. To easily and efficiently observe iron-induced changes, it is important to isolate the iron-fertilized patch from the surrounding unfertilized waters (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 Traon, 2012). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds compared to the surrounding environment with the vertical coherence (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

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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 third consideration for successful OIF experiment is timing which can be broken down into when an experiment starts and how long it lasts. 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).

Duration: 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. 9a) 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. 9b) (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). Among OIF experiments, EIFEX, the second-longest at ~39 days, fully monitored all the phases of the phytoplankton bloom from onset to termination, and it alone observed iron-induced deep export production (Fig. 8a and 9a) (Assmy et al., 2013; Smetacek et al., 2012). It is therefore important to predict both the needed time for onset and the time required for the response to run its full course, otherwise it will not be possible to quantify the net effect.

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, 2008). However, since these small-scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric CO_2 levels, 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 the large uncertainties remaining in the technique mean that potential risks to the environment/ecosystem by even small-scale OIF experiments are not yet well understood. At present, large-scale and/or commercial OIF experiments are banned by international regulation (Williamson et al., 2012). 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. 10) (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, 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: Introduction to the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project

4.1 Background for KIFES

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 data, only OIF experiment with a 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 the 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 the geological evidence of intensive organic carbon burial in the sediments, 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, and represents the fast sinking of diatoms within a short time. Scientists at KOPRI suspect that enhancement of diatom flux might be related to input of bioavailable iron that controls phytoplankton population in the Southern Ocean. In addition, the oceanographic (physical-biogeochemical-geological) parameters might be ascribed to the unique increase of diatom production, the fast sinking rate of the organic matters, and the well preservation of organic carbon in this area. Therefore, it is expected that OIF in diatom-dominated eastern Bransfield Basin will be effective for carbon export. However, the exact driving force for this unique process should be intensively investigated prior to the OIF experiment.

Timely, a science-oriented iron fertilization project, KIFES (Fig. 11), was launched by the Korean oceanographers in 2016 with the research funding supported by the Korean Ministry of Oceans and Fisheries. This project will be led 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 the KIFES project is (1) to further understand the role of iron for atmospheric carbon sequestration in the Southern Ocean, (2) to verify

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proper environmental conditions to maximize effectiveness of OIF experiment, and (3) to reveal short- and long-term side effects derived from artificial OIF experiment.

4.2 KIFES Plans

The KIFES project is 5-year plan project (2016–2020). This project includes two preliminary environmental surveys, a preliminary OIF test, the KIFES OIF experiment, and an assessment of the KIFES project. In this section, we introduce the major goals and main tasks of KIFES project.

4.2.1 First project year (2016-underway)

Goals: Determination of KIFES OIF experiment sites and establishment of an international OIF network

Main tasks: (1) Investigation of earlier OIF locations and experiments to produce a database of physical and biogeochemical parameters from *in situ* observations and remote-sensing data to select appropriate sites and to determine timing for an new OIF experiment in the eastern Bransfield Strait, (2) Preparation of scientific instruments for ocean physical and biogeochemical monitoring, (3) Establishment of an international collaborative OIF network, and (4) KIFES proposal preparation for approval of LC/LP.

4.2.2 Second project year (2017)

Goal: First preliminary survey to provide a foundational understanding of ocean environmental conditions in the eastern Bransfield Strait

Main tasks: (1) Using ice breaker RV *ARAON*, field investigation of physical and biogeochemical parameters, including side effect parameters such as N_2O in the eastern Bransfield Strait – parameters and sites based on the 2016 investigation, and (2) Continued preparation of LC/LP proposal.

4.2.3 Third project year (2018)

Goals: Second preliminary survey and a preliminary test of OIF in eddy structure prior to KIFES

Main tasks: (1) Detection of an eddy using observations from acoustic Doppler current profilers and satellites in the eastern Bransfield Strait, (2) Intensive physical and biogeochemical field investigation in the eddy, (3) Rehearsal of OIF experiment in the eddy structure, and (4) Submission of the LC/LP proposal to obtain approval for the KIFES experiment from International Maritime Organization.

4.2.4 Fourth-year project (2019)

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

Main tasks: (1) The conducting of KIFES, a scientific OIF experiment in an eddy structure in the eastern Bransfield Strait employing underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations, and (2) Assessment for KIFES effects and side effects

4.2.5 Fifth-year project (2020)

Goal: Integrated assessment of the KIFES project

Main tasks: (1) Submission of the OIF assessment report, (2) Submission of scientific results to international journals, (3) Collection of feedback about the KIFES project from international scientific/oceanographic communities, and (4) Preparation of the second stage of the KIFES project.

4.3 Expected results of KIFES

KIFES will be performed after a decade long gap since LOHAFEX. None of the KIFES scientists have any interest in selling carbon credits by conducting OIF experiments. Rather, our interest lies in the detailed investigation of the biogeochemical effects of iron addition in the Southern Ocean and in the OIF evaluation as one of possible geo-engineering methods that might be used to mitigate the realities of the climate change effects we face. We hope that the 5-year KIFES project can give a clear answer as to whether or not OIF is a promising as a geo-engineering solution. The KIFES project will 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. Likewise, international cooperation is essential for the successful performance of KIFES and for improvement of our outlook for the Earth's future.

5 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 greenhouse 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. Therefore, validation and suitability of artificial OIF for mitigation of increasing atmospheric carbon levels has been debated. To fully understand the efficiency, capacity, and risks of OIF, scientifically-based and site-limited OIF experimentation is needed to consider such major factors as amount/patch size associated with iron addition, location, and experiment length, including compliance with international OIF regulations. A timely 5-year iron fertilization project, KIFES was launched in 2016 under the leadership of KOPRI with the support of domestic/international collaborative networks. This project focuses on investigating the details of the biogeochemical responses to artificial iron addition in the Southern Ocean and assessing suitability of OIF as one possible carbon removal strategy under international maritime laws. Previously raised issues associated with the risks of OIF will be investigated during the KIFES project.

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References

Abraham, E. R., Law, C. S., Boyd, P. W., Lavender, S. J., Maldonado, M. T., and Bowie, A. R.: Importance of stirring in the development of an iron-fertilized phytoplankton bloom, Nature, 407, 727-730, 2000.

ACE CRC: Position Analysis: Ocean Fertilisation: Science and Policy Issues, ACE CRC, Hobart, 2008.

ACE CRC: Position Analysis: Ocean Fertilisation, ACE CRC, Hobart, 2015.

Anderson, M. A. and Morel, F. M. M.: The influence of aqueous iron chemistry on the uptake of iron by the coastal diatom *Thalassiosira weissflogii*, Limnol. Oceanogr., 27, 789-813, 1982.

Assessment Framework for Scientific Research Involving Ocean Fertilization, LC 32/15, Annex 6, 2010.

Aono, T., Yamada, M., Kudo, I., Imai, K., Nojiri, Y., and Tsuda, A.: Export fluxes of particulate organic carbon estimated from ^{234}Th/^{238}U disequilibrium during the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS 2001), Prog. Oceanogr., 64, 263-282, 2005.

Assmy, P., Henjes, J., Klaas, C., and Smetacek, V.: Mechanisms determining species dominance in a phytoplankton bloom induced by the iron fertilization experiment EisenEx in the Southern Ocean, Deep-Sea Res. Pt. I, 54, 340-362, 2007.

Assmy, P., Smetacek, V., Montresor, M., Klaas, C., Henjes, J., Strass, V. H., Arrieta, J. M., Bathmann, U., Berg, G. M., Breitbarth, E., Cisewski, B., Friedrichs, L., Fuchs, N., Herndl, G. J., Jansen, S., Krägefsky, S., Latasa, M., Peeken, I., Röttgers, R., Scharek, R., Schüller, S. E., Steigenberger, S., Webb, A., and Wolf-Gladrow, D.: Thick-shelled, grazer-protected diatoms decouple ocean carbon and silicon cycles in the iron-limited Antarctic Circumpolar Current, Proc. Natl. Acad. Sci. USA., 110, 20633-20638, 2013.

Bakker, D. C. E., Bozec, Y., Nightingale, P. D., Goldson, L., Messias, M.-J., de Baar, H. J. W., Liddicoat, M., Skjelvan, I., Strass, V., and Watson, A. J.: Iron and mixing affect biological carbon uptake in SOIREE and EisenEx, two Southern Ocean iron fertilisation experiments, Deep-Sea Res. Pt. I, 52, 1001-1019, 2005.

Bakker, D. C. E., Watson, A. J., and Law, C. S.: Southern Ocean iron enrichment promotes inorganic carbon drawdown, Deep-Sea Res. Pt. II, 48, 2483-2507, 2001.

Bange, H. W.: New Directions: The importance of oceanic nitrous oxide emissions, Atmos. Environ., 40, 198-199, 2006.

Barber, R. T. and Hiscock, M. R.: A rising tide lifts all phytoplankton: Growth response of other phytoplankton taxa in diatom-dominated blooms, Global Biogeochem. Cycles, 20, GB4S03, 2006.

Barnola, J. M., Raynaud, D., Korotkevich, Y. S., and Lorius, C.: Vostok ice core provides 160,000-year record of atmospheric CO_2, Nature, 329, 408-414, 1987.

Behrenfeld, M. J., Bale, A. J., Kolber, Z. S., Aiken, J., and Falkowski, P. G.: Confirmation of Iron Limitation of Phytoplankton Photosynthesis in the Equatorial Pacific-Ocean, Nature, 383, 508-511, 1996.

Berg, G. M., Mills, M. M., Long, M. C., Bellerby, R., Strass, V., Savoye, N., Röttgers, R., Croot, P. L., Webb, A., and Arrigo, K. R.: Variation in particulate C and N isotope composition following iron fertilization in two successive phytoplankton communities in the Southern Ocean, Global Biogeochem. Cycles, 25, GB3013, 2011.

Bidigare, R. R., Hanson, K. L., Buesseler, K. O., Wakeham, S. G., Freeman, K. H., Pancost, R. D., Millero, F. J., Steinberg, P., Popp, B. N., Latasa, M., Landry, M. R., and Laws, E. A.: Iron-stimulated changes in ^{13}C fractionation and export by equatorial Pacific phytoplankton: Toward a paleogrowth rate proxy, Paleoceanography, 14, 589-595, 1999.

Blain, S., Queguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet, C., Brussaard, C., Carlotti, F., Christaki, U., Corbiere, A., Durand, I., Ebersbach, F., Fuda, J.-L., Garcia, N., Gerringa, L., Griffiths, B., Guigue, C., Guillerm, C., Jacquet, S., Jeandel, C., Laan, P., Lefevre, D., Lo Monaco, C., Malits, A., Mosseri, J., Obernosterer, I., Park, Y.-H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., Trull, T., Uitz, J., van Beek, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, L., and Wagener, T.: Effect of natural iron fertilization on carbon sequestration in the Southern Ocean, Nature, 446, 1070-1074, 2007.

Boyd, P. W. and Abraham, E. R.: Iron-mediated changes in phytoplankton photosynthetic competence during SOIREE, Deep-Sea Res. Pt. II, 48, 2529-2550, 2001.

Boyd, P. W., Jickells, T., Law, C. S., Blain, S., Boyle, E. A., Buesseler, K. O., Coale, K. H., Cullen, J. J., de Baar, H. J. W., Follows, M., Harvey, M., Lancelot, C., Levasseur, M., Owens, N. P. J., Pollard, R., Rivkin, R. B., Sarmiento, J., Schoemann, V., Smetacek, V., Takeda, S., Tsuda, A., Turner, S., and Watson, A. J.: Mesoscale Iron Enrichment Experiments 1993-2005: Synthesis and Future Directions, Science, 315, 612-617, 2007.

Boyd, P. W. and Law, C. S.: The Southern Ocean Iron RElease Experiment (SOIREE)—introduction and summary, Deep-Sea Res. Pt. II, 48, 2425-2438, 2001.

Boyd, P. W., Law, C. S., Wong, C. S., Nojiri, Y., Tsuda, A., Levasseur, M., Takeda, S., Rivkin, R., Harrison, P. J., Strzepek, R., Gower, J., McKay, R. M., Abraham, E., Arychuk, M., Barwell-Clarke, J., Crawford, W., Crawford, D., Hale, M., Harada, K., Johnson, K., Kiyosawa, H., Kudo, I., Marchetti, A., Miller, W., Needoba, J., Nishioka, J., Ogawa, H., Page, J., Robert, M., Saito, H., Sastri, A., Sherry, N., Soutar, T., Sutherland, N., Taira, Y., Whitney, F., Wong, S.-K. E., and Yoshimura, T.: The decline and fate of an iron-induced subarctic phytoplankton bloom, Nature, 428, 549-553, 2004.

Boyd, P. W., Strzepek, R., Takeda, S., Jackson, G., Wong, C. S., McKay, R. M., Law, C., Kiyosawa, H., Saito, H., Sherry, N., Johnson, K., Gower, J., and Ramaiah, N.: The evolution and termination of an iron-induced mesoscale bloom in the northeast subarctic Pacific, Limnol. Oceanogr., 50, 1872-1886, 2005.

Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., Bakker, D. C. E., Bowie, A. R., Buesseler, K. O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M. T., McKay, R. M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J.: A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, Nature, 407, 695-702, 2000.

Broecker, W. S.: Ocean chemistry during glacial time, Geochim. Cosmochim. Acta, 46, 1689-1705, 1982.

Broecker, W. S. and Henderson, G. M.: The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes, Paleoceanography, 13, 352-364, 1998.

Buesseler, K. O.: The decoupling of production and particulate export in the surface ocean, Global Biogeochem. Cycles, 12, 297-310, 1998.

Buesseler, K. O., Andrews, J. E., Pike, S. M., and Charette, M. A.: The Effects of Iron Fertilization on Carbon Sequestration in the Southern Ocean, Science, 304, 414-417, 2004.

Buesseler, K. O. and Boyd, P. W.: Will Ocean Fertilization Work?, Science, 300, 67-68, 2003.

Cavagna, A. J., Fripiat, F., Dehairs, F., Wolf-Gladrow, D., Cisewski, B., Savoye, N., Andrè, L., and Cardinal, D.: Silicon uptake and supply during a Southern Ocean iron fertilization experiment (EIFEX) tracked by Si isotopes, Limnol. Oceanogr., 56, 147-160, 2011.

Chisholm, S. W., Falkowski, P. G., and Cullen, J. J.: Dis-Crediting Ocean Fertilization, Science, 294, 309-310, 2001.

Cisewski, B., Strass, V. H., Losch, M., and Prandke, H.: Mixed layer analysis of a mesoscale eddy in the Antarctic Polar Front Zone, J. Geophys. Res., 113, C05017, 2008.

Coale, K. H., Johnson, K. S., Chavez, F. P., Buesseler, K. O., Barber, R. T., Brzezinski, M. A., Cochlan, W. P., Millero, F. J., Falkowski, P. G., Bauer, J. E., Wanninkhof, R. H., Kudela, R. M., Altabet, M. A., Hales, B. E., Takahashi, T., Landry, M. R., Bidigare, R. R., Wang, X., Chase, Z., Strutton, P. G., Friederich, G. E., Gorbunov, M. Y., Lance, V. P., Hilting, A. K., Hiscock, M. R., Demarest, M., Hiscock, W. T., Sullivan, K. F., Tanner, S. J., Gordon, R. M., Hunter, C. N., Elrod, V. A., Fitzwater, S. E., Jones, J. L., Tozzi, S., Koblizek, M., Roberts, A. E., Herndon, J., Brewster, J., Ladizinsky, N., Smith, G., Cooper, D., Timothy, D., Brown, S. L., Selph, K. E., Sheridan, C. C., Twining, B. S., and Johnson, Z. I.: Southern Ocean Iron Enrichment Experiment: Carbon Cycling in High- and Low-Si Waters, Science, 304, 408-414, 2004.

Coale, K. H., Johnson, K. S., Fitzwater, S. E., Blain, S. P. G., Stanton, T. P., and Coley, T. L.: IronEx-I, an *in situ* iron-enrichment experiment: Experimental design, implementation and results, Deep-Sea Res. Pt. II, 45, 919-945, 1998.

Coale, K. H., Johnson, K. S., Fitzwater, S. E., Gordon, R. M., Tanner, S., Chavez, F. P., Ferioli, L., Sakamoto, C., Rogers, P., Millero, F., Steinberg, P., Nightingale, P., Cooper, D., Cochlan, W. P., Landry, M. R., Constantinou, J., Rollwagen, G., Trasvina, A., and Kudela, R.: A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, Nature, 383, 495-501, 1996.

Cooper, D. J., Watson, A. J., and Nightingale, P. D.: Large decrease in ocean-surface CO_2 fugacity in response to *in situ* iron fertilization, Nature, 383, 511-513, 1996.

Croot, P. L., Bluhm, K., Schlosser, C., Streu, P., Breitbarth, E., Frew, R., and Van Ardelan, M.: Regeneration of Fe(II) during EIFeX and SOFeX, Geophys. Res. Lett., 35, L19606, 2008.

Cullen, J. J.: Status of the iron hypothesis after the Open-Ocean Enrichment Experiment[1], Limnol. Oceanogr., 40, 1336-1343, 1995.

Currie, K. I., Macaskill, B., Reid, M. R., and Law, C. S.: Processes governing the carbon chemistry during the SAGE experiment, Deep-Sea Res. Pt. II, 58, 851-860, 2011.

de Baar, H. J. W., Boyd, P. W., Coale, K. H., Landry, M. R., Tsuda, A., Assmy, P., Bakker, D. C. E., Bozec, Y., Barber, R. T., Brzezinski, M. A., Buesseler, K. O., Boyé, M., Croot, P. L., Gervais, F., Gorbunov, M. Y., Harrison, P. J., Hiscock, W. T., Laan, P., Lancelot, C., Law, C. S., Levasseur, M., Marchetti, A., Millero, F. J., Nishioka, J., Nojiri, Y., van Oijen, T., Riebesell, U., Rijkenberg, M. J. A., Saito, H., Takeda, S., Timmermans, K. R., Veldhuis, M. J. W., Waite, A. M., and Wong, C.-S.: Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment, J. Geophys. Res., 110, C09S16, 2005.

De La Rocha, C. L.: The Biological Pump, in: Treatise on Geochemistry update, edited by: Holland, H. D. and Turekian, K. K., Elsevier Pergamon, Oxford, 1-29, 2007.

Duce, R. A. and Tindale, N. W.: Atmospheric transport of iron and its deposition in the ocean, Limnol. Oceanogr., 36, 1715-1726, 1991.

Falkowski, P. G.: Evolution of the nitrogen cycle and its influence on the biological sequestration of CO_2 in the ocean, Nature, 387, 272-275, 1997.

Frost, B. W.: Phytoplankton bloom on iron rations, Nature, 383, 475-476, 1996.

Fuhrman, J. A. and Capone, D. G.: Possible biogeochemical consequences of ocean fertilization, Limnol. Oceanogr., 36, 1951-1959, 1991.

Gervais, F., Riebesell, U., and Gorbunov, M. Y.: Changes in primary productivity and chlorophyll *a* in response to iron fertilization in the Southern Polar Frontal Zone, Limnol. Oceanogr., 47, 1324-1335, 2002.

Harvey, M. J., Law, C. S., Smith, M. J., Hall, J. A., Abraham, E. R., Stevens, C. L., Hadfield, M. G., Ho, D. T., Ward, B., Archer, S. D., Cainey, J. M., Currie, K. I., Devries, D., Ellwood, M. J., Hill, P., Jones, G. B., Katz, D., Kuparinen, J., Macaskill, B., Main, W., Marriner, A., McGregor, J., McNeil, C., Minnett, P. J., Nodder, S. D., Peloquin, J., Pickmere, S., Pinkerton, M. H., Safi, K. A., Thompson, R., Walkington, M., Wright, S. W., and Ziolkowski, L. A.: The SOLAS air–sea gas exchange experiment (SAGE) 2004, Deep-Sea Res. Pt. II, 58, 753-763, 2010.

Hiscock, W. T. and Millero, F. J.: Nutrient and carbon parameters during the Southern Ocean iron experiment (SOFeX), Deep-Sea Res. Pt. I, 52, 2086-2108, 2005.

Hoffmann, L. J., Peeken, I., Lochte, K., Assmy, P., and Veldhuis, M.: Different reactions of Southern Ocean phytoplankton size classes to iron fertilization, Limnol. Oceanogr., 51, 1217-1229, 2006.

IPCC: Climate Change 2014: Mitigation of Climate Change, Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (Eds. O. Edenhofer, R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlömer, C. von Stechow, T. Zwickel, and J. C. Minx), Cambridge Univ. Press, Cambridge, 2014.

IPCC: Climate Change 2013: The Physical Science Basis, Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (Eds. T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley), Cambridge Univ. Press, Cambridge, 2013.

IPCC: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (Eds. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller), Cambridge Univ. Press, Cambridge, 2007.

IPCC: Climate Change 2001: The Scientific Basis, Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change (Eds. D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell, and C. A. Johnson), Cambridge Univ. Press, Cambridge, 2001.

IPCC: Climate Change 1995: The Science of Climate Change, Contribution of Working Group 1 to the Second Assessment Report of the Intergovernmental Panel on Climate Change (Eds. J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg, and K. Maskell), Cambridge Univ. Press, Cambridge, 1995.

IPCC: Climate Change 1992: The Supplementary Report to the IPCC Scientific Assessment (Eds. J. T. Houghton, B. A. Callander, and S. K. Varney), Cambridge Univ. Press, 1992.

IPCC: Climate Change: The IPCC Scientific Assessment of Climate Change (Eds. J. T. Houghton, G. J. Jenkins, and J. J. Ephraums), Cambridge Univ. Press, Cambridge, 1990.

Jin, X. and Gruber, N.: Offsetting the radiative benefit of ocean iron fertilization by enhancing N_2O emissions, Geophys. Res. Lett., 30, 2249, 2003.

Johnson, K. S. and Karl, D. M.: Is Ocean Fertilization Credible and Creditable?, Science, 296, 467-468, 2002.

Kolber, Z. S., Barber, R. T., Coale, K. H., Fitzwateri, S. E., Greene, R. M., Johnson, K. S., Lindley, S., and Falkowski, P. G.: Iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean, Nature, 371, 145-149, 1994.

Koltermann, K. P., Gouretski, V. V., and Jancke, K.: Hydrographic Atlas of the World Ocean Circulation Experiment (WOCE), vol. 3, Atlantic Ocean, edited by M. Sparrow, P. Chapman, and J. Gould, Int. WOCE Proj. Off., Southampton, U. K., 2011.

Kudo, I., Noiri, Y., Cochlan, W. P., Suzuki, K., Aramaki, T., Ono, T., and Nojiri, Y.: Primary productivity, bacterial productivity and nitrogen uptake in response to iron enrichment during the SEEDS II, Deep-Sea Res. Pt. II, 56, 2755-2766, 2009.

Landry, M. R., Constantinou, J., Latasa, M., Brown, S. L., Bidigare, R. R., and Ondrusek, M. E.: Biological response to iron fertilization in the eastern equatorial Pacific (IronEx II). III. Dynamics of phytoplankton growth and microzooplankton grazing, Mar. Ecol. Prog. Ser., 201, 57-72, 2000.

Latasa, M., Henjes, J., Scharek, R., Assmy, P., Röttgers, R., and Smetacek, V.: Progressive decoupling between phytoplankton growth and microzooplankton grazing during an iron-induced phytoplankton bloom in the Southern Ocean (EIFEX), Mar. Ecol. Prog. Ser., 513, 39-50, 2014.

Law, C. S.: Predicting and monitoring the effects of large-scale ocean iron fertilization on marine trace gas emissions, Mar. Ecol. Prog. Ser., 364, 283-288, 2008.

Law, C. S., Crawford, W. R., Smith, M. J., Boyd, P. W., Wong, C. S., Nojiri, Y., Robert, M., Abraham, E. R., Johnson, W. K., Forsland, V., and Arychuk, M.: Patch evolution and the biogeochemical impact of entrainment during an iron fertilisation experiment in the sub-Arctic Pacific, Deep-Sea Res. Pt. II, 53, 2012-2033, 2006.

Law, C. S. and Ling, R. D.: Nitrous oxide flux and response to increased iron availability in the Antarctic Circumpolar Current, Deep-Sea Res. Pt. II, 48, 2509-2527, 2001.

Law, C. S., Smith, M. J., Stevens, C. L., Abraham, E. R., Ellwood, M. J., Hill, P., Nodder, S., Peloquin, J., Pickmere, S., Safi, K., and Walkington, C. M.: Did dilution limit the phytoplankton response to iron addition in HNLCLSi sub-Antarctic waters during the SAGE experiment?, Deep-Sea Res. Pt. II, 58, 786-799, 2011.

Law, C. S., Watson, A. J., Liddicoat, M. I., and Stanton, T.: Sulphur hexafluoride as a tracer of biogeochemical and physical processes in an open-ocean iron fertilisation experiment, Deep-Sea Res. Pt. II, 45, 977-994, 1998.

Lawrence, M. G.: Side Effects of Oceanic Iron Fertilization, Science, 297, 1993, 2002.

Lenton, T. M. and Vaughan, N. E.: The radiative forcing potential of different climate geoengineering options, Atmos. Chem. Phys., 9, 5539-5561, 2009.

Leung, D. Y. C., Caramanna, G., and Maroto-Valer, M. M.: An overview of current status of carbon dioxide capture and storage technologies, Renew. Sust. Energ. Rev., 39, 426-443, 2014.

Levasseur, M., Scarratt, M. G., Michaud, S., Merzouk, A., Wong, C. S., Arychuk, M., Richardson, W., Rivkin, R. B., Hale, M., Wong, E., Marchetti, A., and Kiyosawa, H.: DMSP and DMS dynamics during a mesoscale iron fertilization experiment in the Northeast Pacific—Part I: Temporal and vertical distributions, Deep-Sea Res. Pt. II, 53, 2353-2369, 2006.

Liss, P., Chuck, A., Bakker, D., and Turner, S.: Ocean fertilization with iron: effects on climate and air quality, Tellus B, 57, 269-271, 2005.

London Convention: Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter 1972, 1972.

London Protocol: 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972, 1996.

Marshall, J. and Speer, K.: Closure of the meridional overturning circulation through Southern Ocean upwelling, Nat. Geosci., 5, 171-180, 2012.

Martin, J. H.: Glacial-interglacial CO_2 change: The Iron Hypothesis, Paleoceanography, 5, 1-13, 1990.

Martin, J. H. and Chisholm, P.: Design for a mesoscale iron enrichment experiment. Woods Hole Oceanographic Institution,U.S JGOFS Planning Report, 15, 1992.

Martin, J. H., Coale, K. H., Johnson, K. S., Fitzwater, S. E., Gordon, R. M., Tanner, S. J., Hunter, C. N., Elrod, V. A., Nowicki, J. L., Coley, T. L., Barber, R. T., Lindley, S., Watson, A. J., Van Scoy, K., Law, C. S., Liddicoat, M. I., Ling, R., Stanton, T., Stockel, J., Collins, C., Anderson, A., Bidigare, R., Ondrusek, M., Latasa, M., Millero, F. J., Lee, K., Yao, W., Zhang, J. Z., Friederich, G., Sakamoto, C., Chavez, F., Buck, K., Kolber, Z., Greene, R., Falkowski, P., Chisholm, S. W., Hoge, F., Swift, R., Yungel, J., Turner, S., Nightingale, P., Hatton, A., Liss, P., and Tindale, N. W.: Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean, Nature, 371, 123-129, 1994.

Martin, J. H. and Fitzwater, S. E.: Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic, Nature, 331, 341-343, 1988.

Martin, P., van der Loeff, M. R., Cassar, N., Vandromme, P., d'Ovidio, F., Stemmann, L., Rengarajan, R., Soares, M., González, H. E., Ebersbach, F., Lampitt, R. S., Sanders, R., Barnett, B. A., Smetacek, V., and Naqvi, S. W. A.: Iron fertilization enhanced net community production but not downward particle flux during the Southern Ocean iron fertilization experiment LOHAFEX, Global Biogeochem. Cycles, 27, 871-881, 2013.

Matthews, B.: Climate engineering: a critical review of proposals, their scientific and political context, and possible impacts, Compiled for scientists for global responsibility, 1996. ⟨http://records.viu.ca/earles/geol312o/assignments/mitigation.htm⟩.

McElroy, M. B.: Marine biological controls on atmospheric CO_2 and climate, Nature, 302, 328-329, 1983.

Ming, T., de_Richter, R., Liu, W., and Caillol, S.: Fighting global warming by climate engineering: Is the Earth radiation management and the solar radiation management any option for fighting climate change?, Renew. Sust. Energ. Rev., 31, 792-834, 2014.

Mitchell, B. G., Brody, E. A., Holm-Hansen, O., McClain, C., and Bishop, J.: Light limitation of phytoplankton biomass and macronutrient utilization in the Southern Ocean, Limnol. Oceanogr., 36, 1662-1677, 1991.

Moore, J. K., Doney, S. C., Glover, D. M., and Fung, I. Y.: Iron cycling and nutrient-limitation patterns in surface waters of the world ocean, Deep-Sea Res. Pt. II, 49, 463-507, 2002.

Morel, F. M. M. and Price, N. M.: The Biogeochemical Cycles of Trace Metals in the Oceans, Science, 300, 944-947, 2003.

Morrow, R. and Le Traon, P.-Y.: Recent advances in observing mesoscale ocean dynamics with satellite altimetry, Adv. Space Res., 50, 1062-1076, 2012.

Nagao, I., Hashimoto, S., Suzuki, K., Toda, S., Narita, Y., Tsuda, A., Saito, H., Kudo, I., Kato, S., Kajii, Y., and Uematsu, M.: Responses of DMS in the seawater and atmosphere to iron enrichment in the subarctic western North Pacific (SEEDS-II), Deep-Sea Res. Pt. II, 56, 2899-2917, 2009.

Neftel, A., Oeschger, H., Schwander, J., Stauffer, B., and Zumbrunn, R.: Ice core sample measurements give atmospheric CO_2 content during the past 40,000 yr, Nature, 295, 220-223, 1982.

Nishioka, J., Takeda, S., Baar, H. J. W. D., Croot, P. L., Boye, M., Laan, P., and Timmermans, K. R.: Changes in the concentration of iron in different size fractions during an iron enrichment experiment in the open Southern Ocean, Mar. Chem., 95, 51-63, 2005.

Nodder, S. D., Charette, M. A., Waite, A. M., Trull, T. W., Boyd, P. W., Zeldis, J., and Buesseler, K. O.: Particle transformations and export flux during an *in situ* iron-stimulated algal bloom in the Southern Ocean, Geophys. Res. Lett., 28, 2409-2412, 2001.

Peloquin, J., Hall, J., Safi, K., Ellwood, M., Law, C. S., Thompson, K., Kuparinen, J., Harvey, M., and Pickmere, S.: Control of the phytoplankton response during the SAGE experiment: A synthesis, Deep-Sea Res. Pt. II, 58, 824-838, 2011.

Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J. M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399, 429-436, 1999.

Pollard, R. T., Salter, I., Sanders, R. J., Lucas, M. I., Moore, C. M., Mills, R. A., Statham, P. J., Allen, J. T., Baker, A. R., Bakker, D. C. E., Charette, M. A., Fielding, S., Fones, G. R., French, M., Hickman, A. E., Holland, R. J., Hughes, J. A., Jickells, T. D., Lampitt, R. S., Morris, P. J., Nedelec, F. H., Nielsdottir, M., Planquette, H., Popova, E. E., Poulton, A. J., Read, J. F., Seeyave, S., Smith, T., Stinchcombe, M., Taylor, S., Thomalla, S., Venables, H. J., Williamson, R., and Zubkov, M. V.: Southern Ocean deep-water carbon export enhanced by natural iron fertilization, Nature, 457, 577-580, 2009.

Rees, A. P., Nightingale, P. D., Owens, N. J. P., and Team, P. F.: FeeP—An *in situ* PO_4^{3-} and Fe^{2+} addition experiment to waters of the sub-tropical north-east Atlantic, Geophys. Res. Abstr., 9, 2007.

Resolution LC-LP.1 (2008) on the Regulation of Ocean Fertilization, LC 30/16, Annex 6, 2008.

Resolution LP.4 (8) on the Amendment to the London Protocol to Regulate the Placement of Matter for Ocean Fertilization and Other Marine Geoengineering Activities, LP.8, LC 35/15, Annex 4, Annex 5, 2013.

Sarmiento, J. L. and Gruber, N.: Ocean Biogeochemical Dynamics, Princeton University Press, 2006.

Sarmiento, J. L. and Orr, J. C.: Three-dimensional simulations of the impact of Southern Ocean nutrient depletion on atmospheric CO_2 and ocean chemistry, Limnol. Oceanogr., 36, 1928-1950, 1991.

Sigman, D. M. and Boyle, E. A.: Glacial/interglacial variations in atmospheric carbon dioxide, Nature, 407, 859-869, 2000.

Silver, M. W., Bargu, S., Coale, S. L., Benitez-Nelson, C. R., Garcia, A. C., Roberts, K. J., Sekula-Wood, E., Bruland, K. W., and Coale, K. H.: Toxic diatoms and domoic acid in natural and iron enriched waters of the oceanic Pacific, Proc. Natl. Acad. Sci. USA., 107, 20762-20767, 2010.

Smetacek, V.: EisenEx: International Team Conducts Iron Experiment In Southern Ocean, U.S. JGOFS News, 11, 11–14, 2001.

Smetacek, V.: Ocean iron fertilization experiments: The dawn of a new era in applied ocean sciences?, KOPRI, Korea, 2015.

Smetacek, V., Bathmann, U., and Helmke, E.: The expeditions Antarktis XXI/3-4-5 of the Research Vessel "Polarstern" in 2004. Reports on Polar and Marine Research 500, 2005.

Smetacek, V., Klaas, C., Strass, V. H., Assmy, P., Montresor, M., Cisewski, B., Savoye, N., Webb, A., d/'Ovidio, F., Arrieta, J. M., Bathmann, U., Bellerby, R., Berg, G. M., Croot, P., Gonzalez, S., Henjes, J., Herndl, G. J., Hoffmann, L. J., Leach, H., Losch, M., Mills, M. M., Neill, C., Peeken, I., Rottgers, R., Sachs, O., Sauter, E., Schmidt, M. M., Schwarz, J., Terbruggen, A., and Wolf-Gladrow, D.: Deep carbon export from a Southern Ocean iron-fertilized diatom bloom, Nature, 487, 313-319, 2012.

Smetacek, V. and Naqvi , S. W. A.: The expedition of the research vessel "Polarstern" to the Antarctic in 2009 (ANT-XXV/3 - LOHAFEX), Berichte zur Polar- und Meeresforschung (Reports on Polar and Marine Research). Bremerhaven, Alfred Wegener Institute for Polar and Marine Research, 613, 2010.

Smetacek, V. and Naqvi, S. W. A.: The next generation of iron fertilization experiments in the Southern Ocean, Philos. Trans. A Math. Phys. Eng. Sci., 366, 3947-3967, 2008.

Solomon, S., Garcia, R. R., and Ravishankara, A. R.: On the role of iodine in ozone depletion, J. Geophys. Res., 99, 20491-20499, 1994.

Spolaor, A., Vallelonga, P., Cozzi, G., Gabrieli, J., Varin, C., Kehrwald, N., Zennaro, P., Boutron, C., and Barbante, C.: Iron speciation in aerosol dust influences iron bioavailability over glacial-interglacial timescales, Geophys. Res. Lett., 40, 1618-1623, 2013.

Steinberg, P. A., Millero, F. J., and Zhu, X.: Carbonate system response to iron enrichment, Mar. Chem., 62, 31-43, 1998.

Strong, A.L., Cullen, J. J., and Chisholm, S. W.: Ocean fertilization: Science, policy, and commerce. Oceanography, 22, 236–261, 2009.

Takeda, S. and Tsuda, A.: An *in situ* iron-enrichment experiment in the western subarctic Pacific (SEEDS): Introduction and summary, Prog. Oceanogr., 64, 95-109, 2005.

Talley, L. D.: Hydrographic Atlas of the World Ocean Circulation Experiment (WOCE), Volume 2: Pacific Ocean (eds. Sparrow, M., Chapman, P., and Gould, J.), International WOCE Project Office, Southampton, U.K., ISBN 0-904175-54-5, 2007.

Thiele, S., Fuchs, B. M., Ramaiah, N., and Amann, R.: Microbial Community Response during the Iron Fertilization Experiment LOHAFEX, Appl. Environ. Microbiol., 78, 8803-8812, 2012.

Tréguer, P., Nelson, D. M., Van Bennekom, A. J., DeMaster, D. J., Leynaert, A., and Quéguiner, B.: The Silica Balance in the World Ocean: A Reestimate, Science, 268, 375-379, 1995.

Trick, C. G., Bill, B. D., Cochlan, W. P., Wells, M. L., Trainer, V. L., and Pickell, L. D.: Iron enrichment stimulates toxic diatom production in high-nitrate, low-chlorophyll areas, Proc. Natl. Acad. Sci. USA., 107, 5887-5892, 2010.

Tsuda, A., Kiyosawa, H., Kuwata, A., Mochizuki, M., Shiga, N., Saito, H., Chiba, S., Imai, K., Nishioka, J., and Ono, T.: Responses of diatoms to iron-enrichment (SEEDS) in the western subarctic Pacific, temporal and spatial comparisons, Prog. Oceanogr., 64, 189-205, 2005.

Tsuda, A., Takeda, S., Saito, H., Nishioka, J., Kudo, I., Nojiri, Y., Suzuki, K., Uematsu, M., Wells, M. L., Tsumune, D., Yoshimura, T., Aono, T., Aramaki, T., Cochlan, W. P., Hayakawa, M., Imai, K., Isada, T., Iwamoto, Y., Johnson, W. K., Kameyama, S., Kato, S., Kiyosawa, H., Kondo, Y., Levasseur, M., Machida, R. J., Nagao, I., Nakagawa, F., Nakanishi, T., Nakatsuka, S., Narita, A., Noiri, Y., Obata, H., Ogawa, H., Oguma, K., Ono, T., Sakuragi, T., Sasakawa, M., Sato, M., Shimamoto, A., Takata, H., Trick, C. G., Watanabe, Y. W., Wong, C. S., and Yoshie, N.: Evidence for the grazing hypothesis: Grazing reduces phytoplankton responses of the HNLC ecosystem to iron enrichment in the western subarctic pacific (SEEDS II), J. Oceanogr., 63, 983-994, 2007.

Tsuda, A., Takeda, S., Saito, H., Nishioka, J., Nojiri, Y., Kudo, I., Kiyosawa, H., Shiomoto, A., Imai, K., Ono, T., Shimamoto, A., Tsumune, D., Yoshimura, T., Aono, T., Hinuma, A., Kinugasa, M., Suzuki, K., Sohrin, Y., Noiri, Y., Tani, H., Deguchi, Y., Tsurushima, N., Ogawa, H., Fukami, K., Kuma, K., and Saino, T.: A Mesoscale Iron Enrichment in the Western Subarctic Pacific Induces a Large Centric Diatom Bloom, Science, 300, 958-961, 2003.

Tsumune, D., Nishioka, J., Shimamoto, A., Takeda, S., and Tsuda, A.: Physical behavior of the SEEDS iron-fertilized patch by sulphur hexafluoride tracer release, Prog. Oceanogr., 64, 111-127, 2005.

Tsumune, D., Nishioka, J., Shimamoto, A., Watanabe, Y. W., Aramaki, T., Nojiri, Y., Takeda, S., Tsuda, A., and Tsubono, T.: Physical behaviors of the iron-fertilized patch in SEEDS II, Deep-Sea Res. Pt. II, 56, 2948-2957, 2009.

Turner, S. M., Harvey, M. J., Law, C. S., Nightingale, P. D., and Liss, P. S.: Iron-induced changes in oceanic sulfur biogeochemistry, Geophys. Res. Lett., 31, L14307, 2004.

Turner, S. M., Nightingale, P. D., Spokes, L. J., Liddicoat, M. I., and Liss, P. S.: Increased dimethyl sulphide concentrations in sea water from *in situ* iron enrichment, Nature, 383, 513-517, 1996.

Vaughan, N. E. and Lenton, T. M.: A review of climate geoengineering proposals, Clim. Change, 109, 745-790, 2011.

Volk, T. and Hoffert, M. I.: Ocean Carbon Pumps: Analysis of Relative Strengths and Efficiencies in Ocean-Driven Atmospheric CO_2 Changes, in: The Carbon Cycle and Atmospheric CO2: Natural Variations Archean to Present, edited, Geophys. Monogr. Ser, 99-110, 1985.

Walter, S., Peeken, I., Lochte, K., Webb, A., and Bange, H. W.: Nitrous oxide measurements during EIFEX, the European Iron Fertilization Experiment in the subpolar South Atlantic Ocean, Geophys. Res. Lett., 32, L23613, 2005.

Wanninkhof, R. and Thoning, K.: Measurement of fugacity of CO_2 in surface water using continuous and discrete sampling methods, Mar. Chem., 44, 189-204, 1993.

Watson, A. J., Bakker, D. C. E., Ridgwell, A. J., Boyd, P. W., and Law, C. S.: Effect of iron supply on Southern Ocean CO_2 uptake and implications for glacial atmospheric CO_2, Nature, 407, 730-733, 2000.

Westberry, T. K., Behrenfeld, M. J., Milligan, A. J., and Doney, S. C.: Retrospective satellite ocean color analysis of purposeful and natural ocean iron fertilization, Deep-Sea Res. Pt. I, 73, 1-16, 2013.

Williamson, P., Wallace, D. W. R., Law, C. S., Boyd, P. W., Collos, Y., Croot, P., Denman, K., Riebesell, U., Takeda, S., and Vivian, C.: Ocean fertilization for geoengineering: A review of effectiveness, environmental impacts and emerging governance, Process Saf. Environ. Protect., 90, 475-488, 2012.

Wingenter, O. W., Haase, K. B., Strutton, P., Friederich, G., Meinardi, S., Blake, D. R., and Rowland, F. S.: Changing concentrations of CO, CH_4, C_5H_8, CH_3Br, CH_3I, and dimethyl sulfide during the Southern Ocean Iron Enrichment Experiments, Proc. Nat. Acad. Sci. U.S.A., 101, 8537-8541, 2004.

Wong, C. S., Timothy, D. A., Law, C. S., Nojiri, Y., Xie, L., Wong, S.-K. E., and Page, J. S.: Carbon distribution and fluxes during the SERIES iron fertilization experiment with special reference to the fugacity of carbon dioxide (fCO_2), Deep-Sea Res. Pt. II, 53, 2053-2074, 2006.

Zhuang, G. and Duce, R. A.: The adsorption of dissolved iron on marine aerosol particles in surface waters of the open ocean, Deep-Sea Res. Pt. I, 40, 1413-1429, 1993.

Zhuang, G., Yi, Z., Duce, R. A., and Brown, P. R.: Link between iron and sulphur cycles suggested by detection of Fe(II) in remote marine aerosols, Nature, 355, 537-539, 1992.

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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) ②112 (3) ③112 (7)	0.02	2.00 1.00 1.00	SF_6	72	17	HNLC
3	SOIREE	Feb 1999	61° S 141° E Southern Ocean- Australasian-Pacific sector	RV *Astrolab*	①768 (0) ②312 (3) ③312 (5) ④353 (7)	0.08	3.80 2.60 2.60 2.50	SF_6	50	13	HNLC
4	EisenEx	Nov 2000	48° S, 21° E Southern Ocean- Atlantic sector	RV *Polarstern*	①780 (0) ②780 (7) ③780 (16)	0.06	2.00	SF_6	50	23	HNLC
5	SEEDS-1	Jul–Aug 2001	48.5° N, 165° E North Pacific- 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 Southern Ocean- Atlantic sector	RV *Revelle* RV *Melville*	①631 (0) ②631 (5) ③450 (30)		1.20	SF_6	225	40	HNLCLSi
7	SOFeX-S	Jan–Feb 2002	66.45° S, 171.8° W Southern Ocean- Atlantic sector	RV *Revelle* RV *Melville* RV *Polar star*	①315 (0) ②315 (4) ③315 (7) ④315 (11)		0.70	SF_6	225	28	HNLC
8	SERIES	Jul-Aug 2002	50.14° N, 144.75° W North Pacific- Eastern subarctic Pacific	RV *John P. Tully* RV *El Puma* RV *Kaiyo Maru*	①315 (0) ②315 (6)	<0.10	2.00 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 Southern Ocean-Atlantic sector	RV *Polarstern*	①1406 (0) ②1406 (13)	0.20	1.50 0.34		167	39	HNLC
10	FeeP	Apr–May 2004	27.5° N 22.5° W North Atlantic-Subtropical north-east Atlantic	RV *Charles Darwin* RV *Poseidon*	①1840 (0)	0.20	3.00	SF_6	25	21	LNLC
11	SAGE	Mar–Apr 2004	46.7° S 172.5° E Southern Ocean-Southeast of New Zealand	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
12	SEEDS-2	Jul–Aug 2004	48° N, 166° E North Pacific-Western subarctic gyre	RV *Hakuho-Maru* RV *Kilo-Moana*	①332 (0) ②159 (6)	0.17	1.38	SF_6	64	26	HNLC
13	LOHAFEX	Jan–Mar 2009	48° S, 15° W Southern Ocean-Atlantic sector	RV *Polarstern*	①2000 (0) ②2000 (21)		2.00	SF_6	300	40	HNLCLSi
1	CROZEX*	Nov 2004–Jan 2005	44° S, 50° E Southern Ocean-South of sub-Antarctic Front	RV *Discovery*		0.04	0.55				HNLC
2	KEOPS*	Jan–Feb 2005	50° S, 73° E 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.

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Table 2. Changes of chemical parameters from initial to after concentrations by OIF experiments. Note that *ΔDIC represents changes in DIC concentrations (i.e., $[DIC]_{post\text{-}fertilization} - [DIC]_{pre\text{-}fertilization}$).

	Experiment	Initial NO_3 (μM)	After NO_3 (μM)	Initial PO_4 (μM)	After PO_4 (μM)	Initial Si (μM)	After Si (μM)	Initial pCO_2 (ppm)	After pCO_2 (ppm)	*ΔDIC (μM)
1	IronEx-1	10.8	10.1	0.92	0.90	3.9	3.88	471	458	-6
2	IronEx-2	10.4	6.4	0.80	0.55	5.1	1.1	538	465	-27
3	SOIREE	25.0	22.0	1.50		10.0	7.0	350	312–318	-(18–15)
4	EisenEx	22.0	21.0	1.60	1.5	10.0	10.0	360	340–342	-(15–12)
5	SEEDS-1	18.5	2.7		0.44	31.8	5.0	390	260	-58
6	SOFeX-N	21.9	20.5	1.40	1.31	2.5	1.4	367	341	-13
7	SOFeX-S	26.3	22.8	1.87	1.66	62.8	58.8	365	329	-21
8	SERIES	10.0–12.0	3.0	>1.00	<0.50	14.0–16.0	<2.0	350	265	-36
9	EIFEX	25.0	23.5	1.80	1.50	19.0	8.0	360	330	-13.5
10	FeeP	<0.01		0.01						<-1
11	SAGE	7.9–10.3	11.8	0.62–0.85		0.83–0.97		330	338	25
12	SEEDS-2	18.4	12.7			36.1		370	364	
13	LOHAFEX	20.0	17.5	1.30	1.10	0.50–1.40				

Sources are as follow: Martin et al., 1994; Steinberg et al., 1998; Boyd et al., 2000; Bakker 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 3. 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.

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 distributions were presented 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. Pictures for iron addition procedures: (a) Iron(II) sulfate of 7000 kg, (b) hydrochloric acid, (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). (f) Discharging of Iron(II) sulfate (http://www.geoengineeringmonitor.org/reasons-to-oppose/).

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 (ΔNitrate = $[NO_3^-]_{post\text{-}fertilization} - [NO_3^-]_{pre\text{-}fertilization}$; 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. (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. 10. Assessment framework for scientific research involving ocean fertilization (OF) (modified from Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).

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).

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Fig. 1

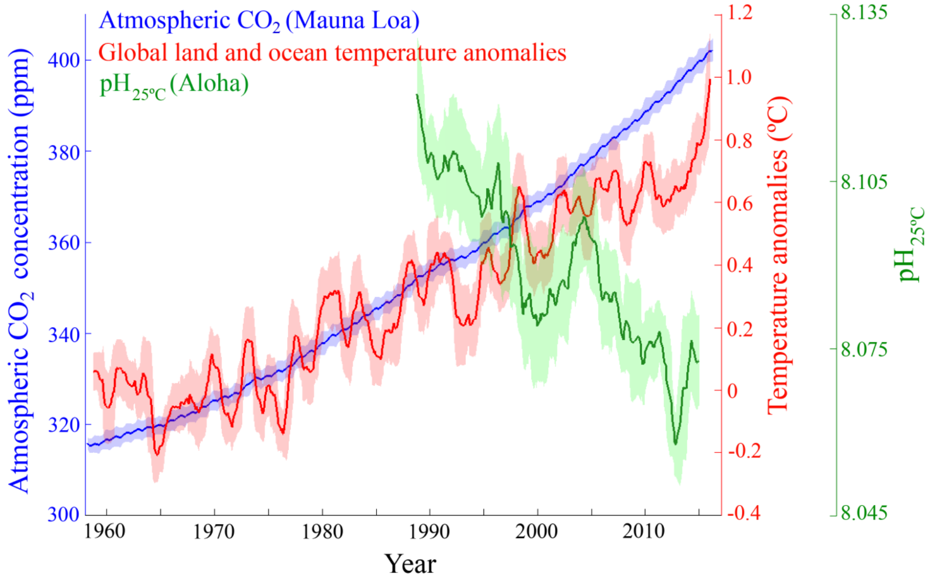

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Fig. 2

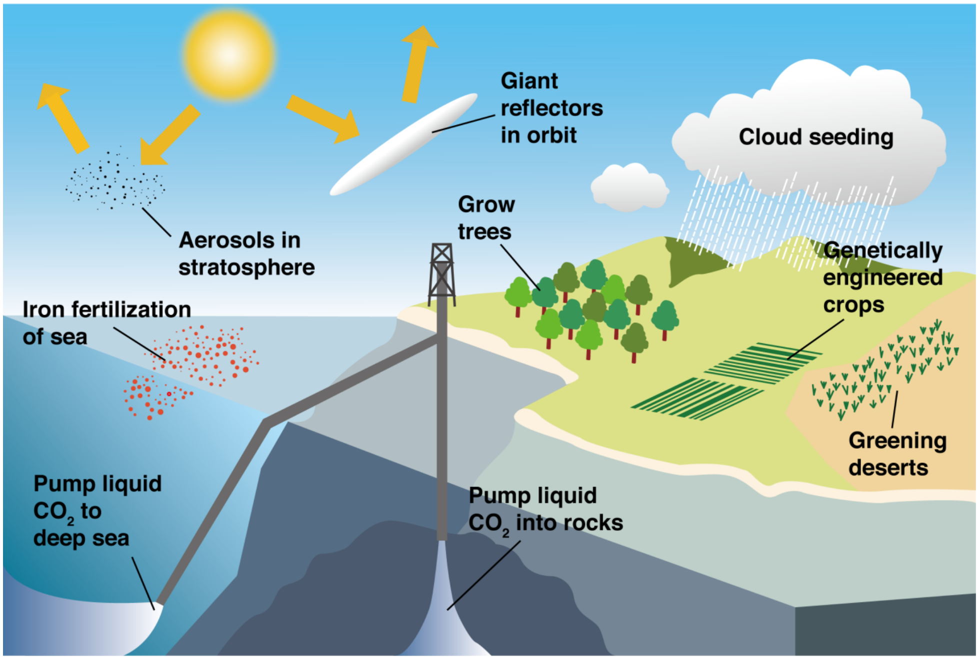

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Fig. 3

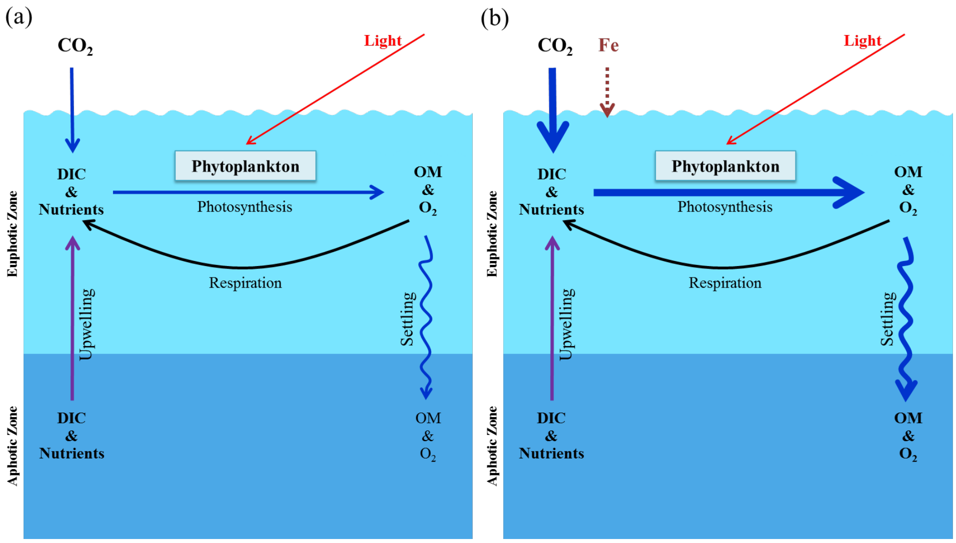

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Fig. 4

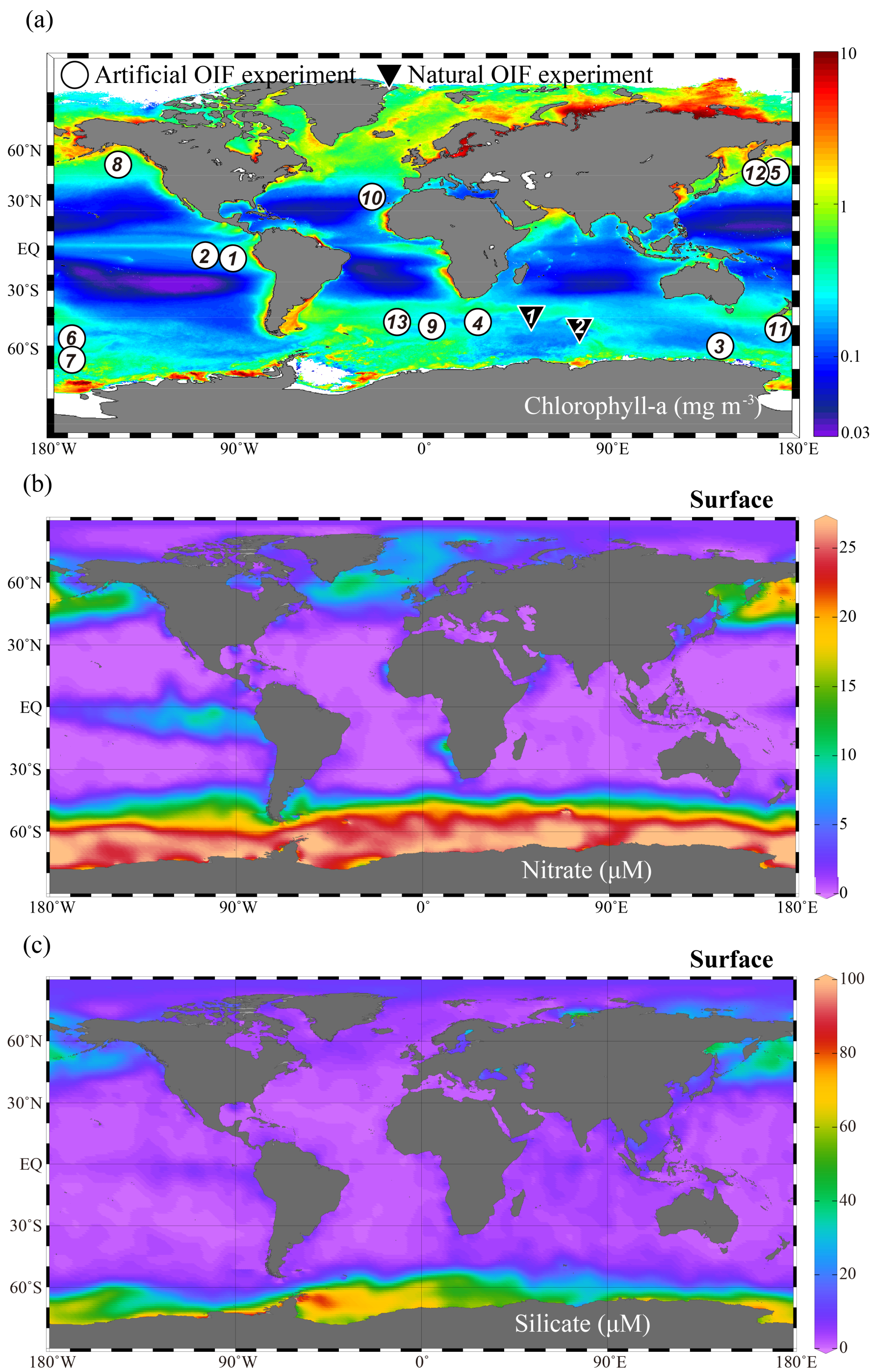

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Fig. 5

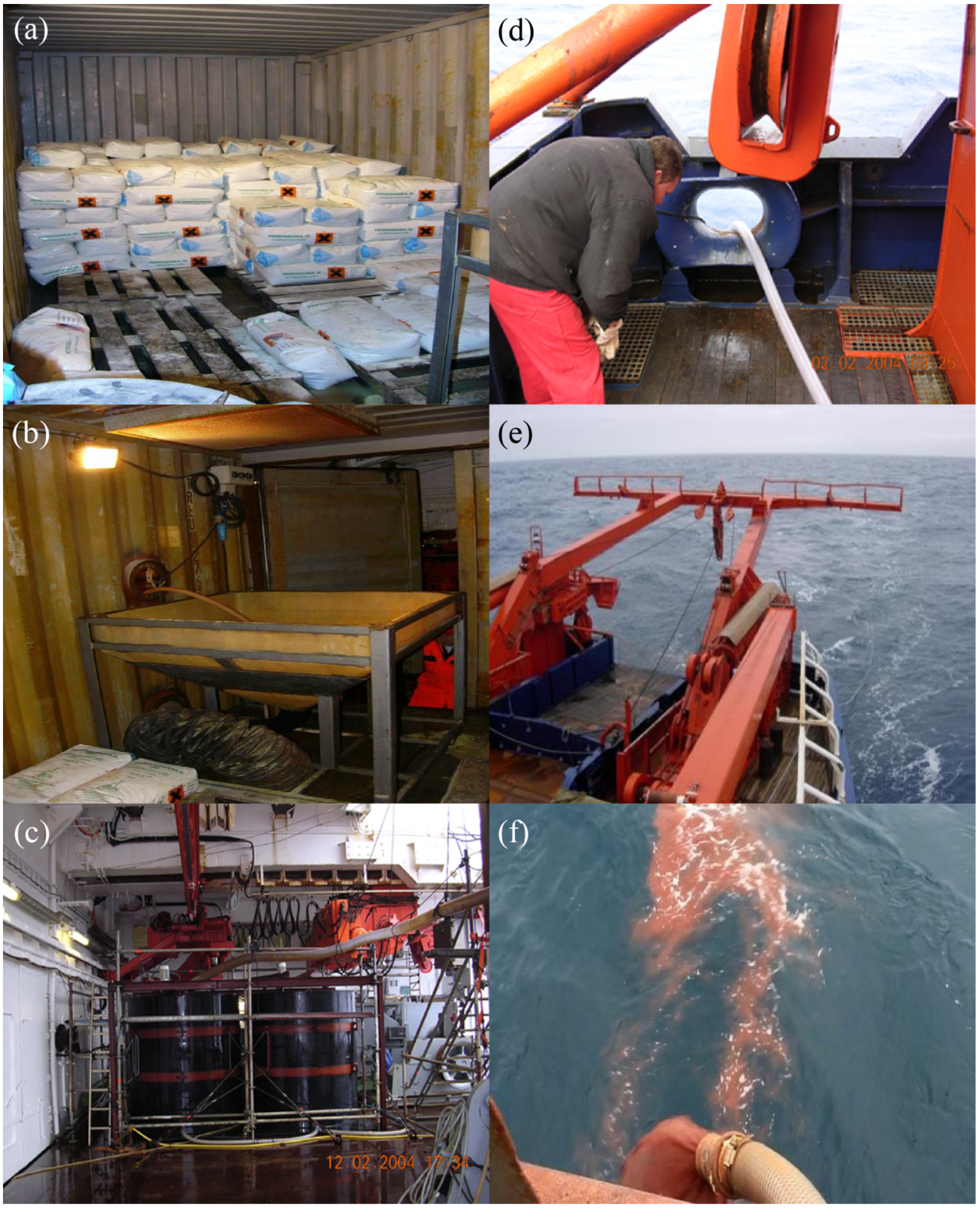

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Fig. 6

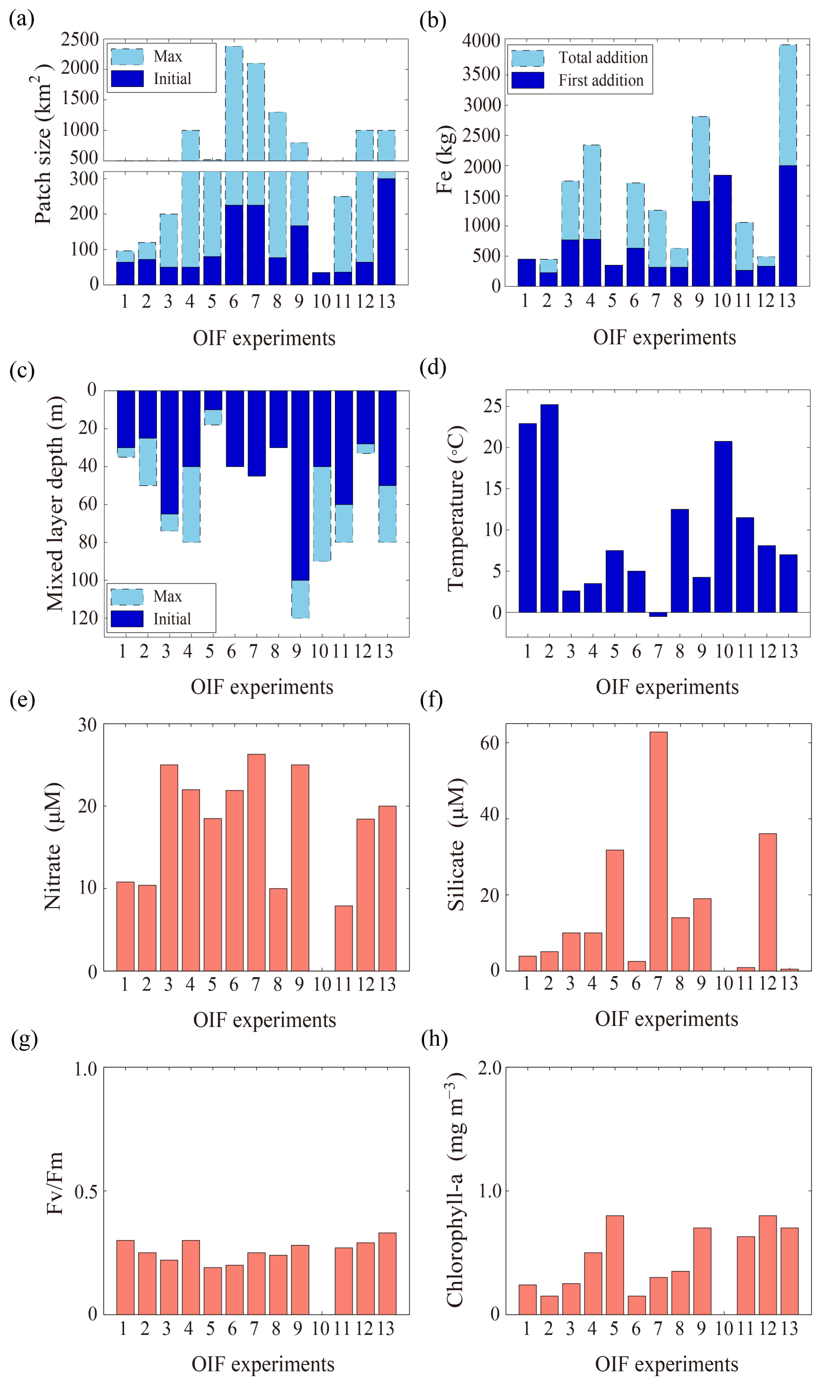

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Fig. 7

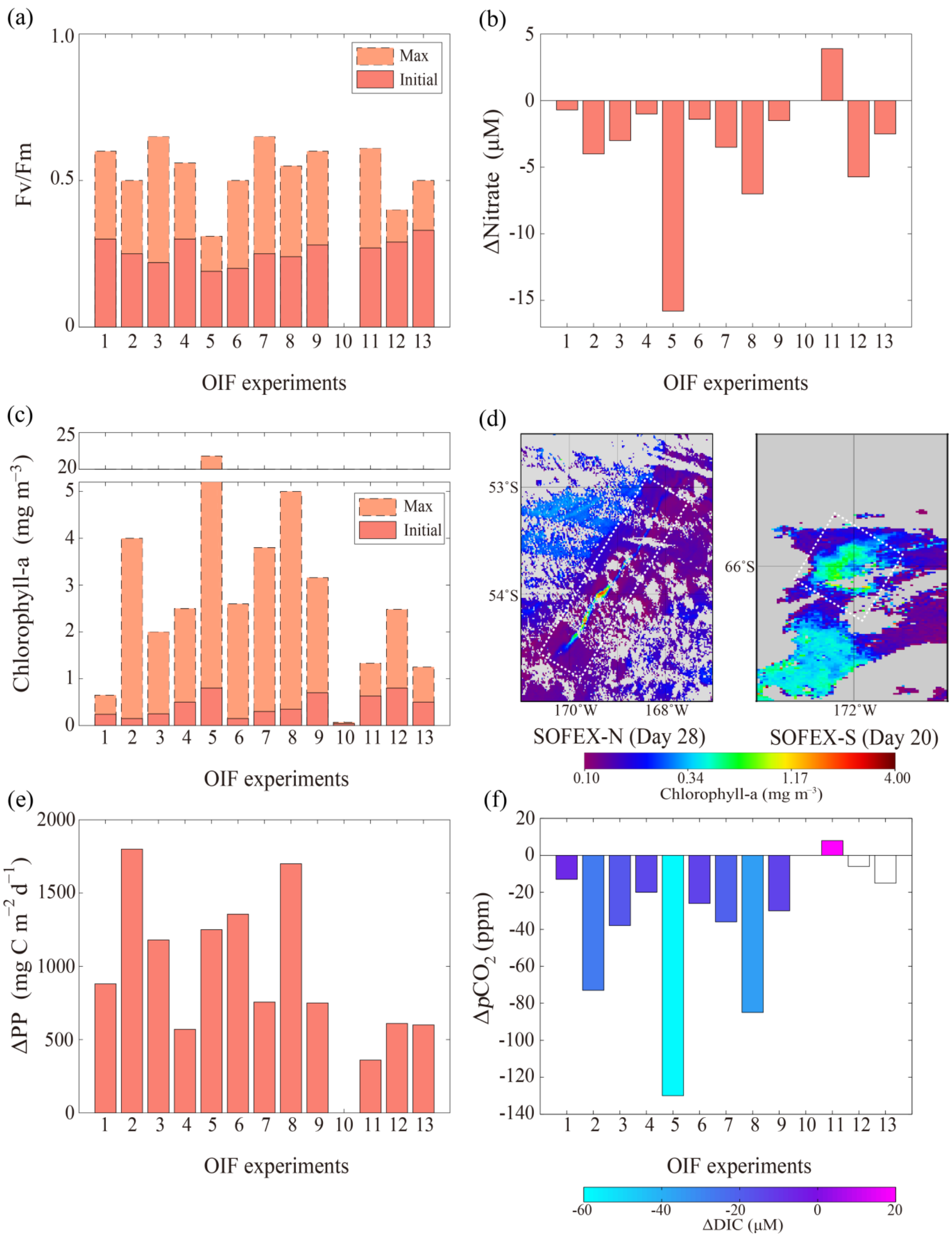

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Fig. 8

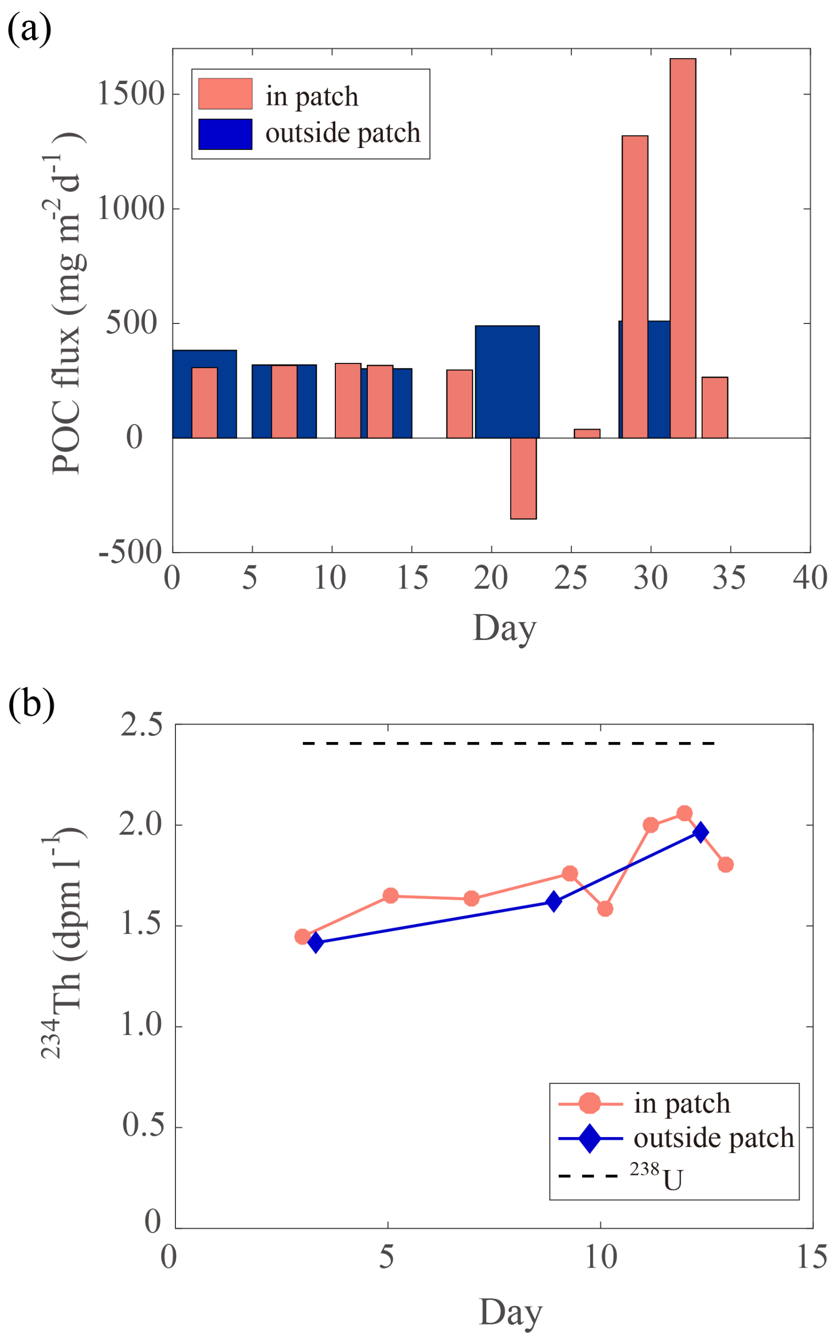

Fig. 9

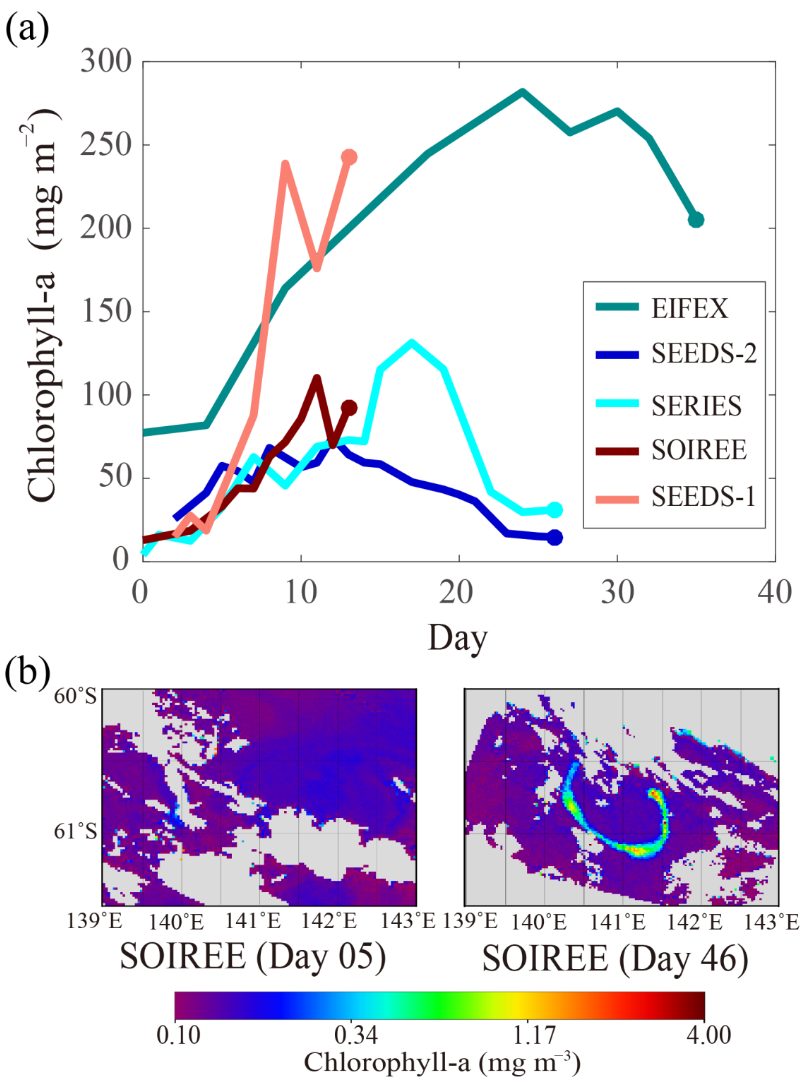
(a)
Chlorophyll-a (mg m^-2)
300
250
200
150
100
50
0
0
10
20
30
40
Day
EIFEX
SEEDS-2
SERIES
SOIREE
SEEDS-1
(b)
60°S
61°S
139°E 140°E 141°E 142°E 143°E
139°E 140°E 141°E 142°E 143°E
SOIREE (Day 05)
SOIREE (Day 46)
0.10
0.34
1.17
4.00
Chlorophyll-a (mg m^-3)

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Fig. 10

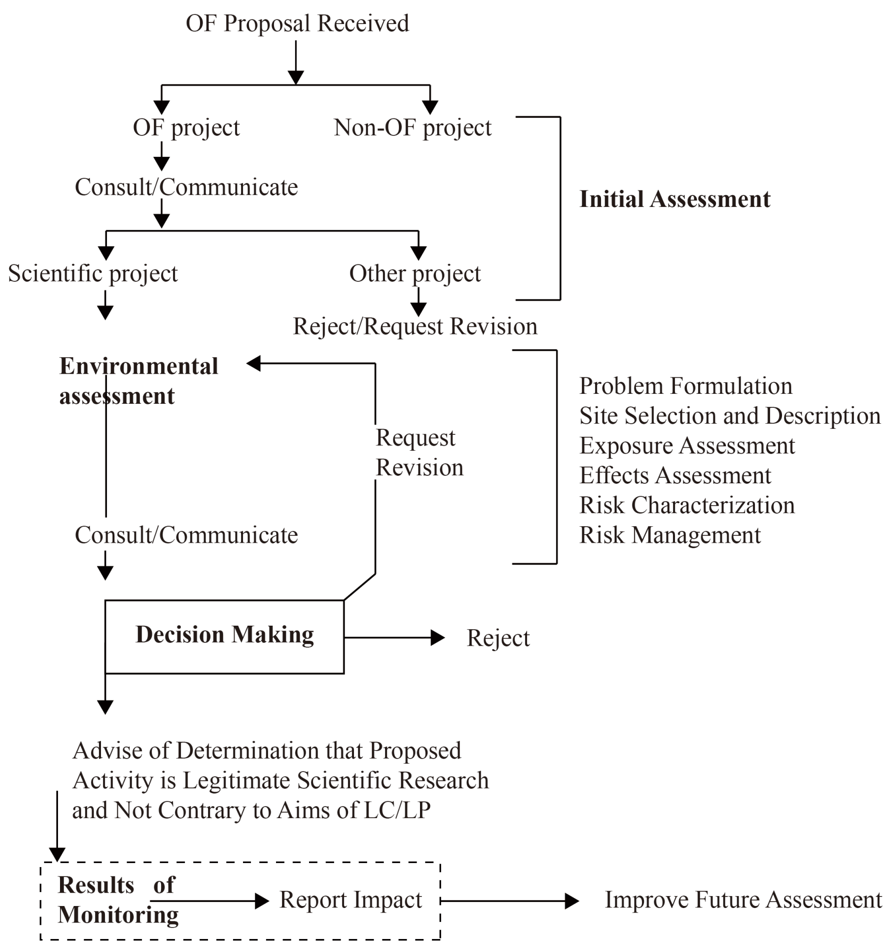

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Fig. 11