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Iron-Stimulated Phytoplankton Blooms in the Southern Ocean: a Brief Review

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Abstract

Nine iron fertilization experiments have been carried out in the Southern Ocean (SO) so far comprising of seven artificial fertilization and two naturally enriched events. The first artificial iron addition, SOIREE, was conducted south of the polar front in February 1999 followed by six more experiments (EisenEx, SOFeX-N, SOFeX-S, EIFEX, SOLAS-SAGE, and LOHAFEX) took place in different sectors of the SO involving multinational and trans-disciplinary efforts. Besides, two naturally fertilized studies (KEOPS and CROZEX) were carried out in the downstream of the SO islands. This article summarizes the significant findings of all the iron-enrichment experiments carried out in the SO and explains the phytoplankton bloom dynamics as observed by satellite data and recapitulates the possible sources of iron entrainment to the water column. Findings from the earlier artificial ocean fertilization experiments revealed strong influence of iron on phytoplankton biomass, community composition, and export production in the SO. Satellite-derived chlorophyll-a concentrations (2002–2016) are utilized to characterize the monthly evolution of phytoplankton blooms in the SO. Results suggest that the areal extent of the bloom varied from 1.1 to 18.1 million km^2 during July (austral winter) and January (austral summer), respectively. The blooms are pronounced in a conducive environment with the optimal light condition, sedimentary source of iron from shallow bathymetric region (< 1 km), continental dust advection, and supply of iron from the marginal ice zone through sea-ice melting. In toto, the SO contributes up to 60% of global ocean phytoplankton blooms during December and January (austral summer), and the dominant region of bloom occurrence is located in the Atlantic sector of the SO, which could be ascribed to iron-rich dust input from Patagonia and regional physical processes.

Keywords Phytoplankton bloom · Iron fertilization · Biogeochemistry · Southern Ocean

1 Introduction

The significance of oceanic phytoplankton in modulating global biogeochemical cycle and climate change is unprecedented. Phytoplankton is the base of the oceanic food-web, supplying organic matter for all higher trophic level marine organisms. They not only imitate the chemical composition of the ocean ecosystem but create it [31]. By determining the phytoplankton productivity (PP) or primary productivity (conversion of inorganic materials into organic matter by phytoplankton), researchers can quantify the amount of CO$_2$ being sequestered from the atmosphere [31]. Research findings indicate that although the ocean's phytoplankton account for < 1% of the photosynthetic biomass on the Earth, phytoplankton contribute almost 50% of the world's total primary production (combining ocean and land) by transforming nearly 45–50 billion tonnes of inorganic carbon into their cells [32], which upon death and decay sinks down to the ocean interior to be deposited in the seafloor sediments. This process is termed as "biological pump." It is reported that phytoplankton and other organisms in the sunlit layer pump about 15% of the organic material synthesized each year to the deep ocean (beyond 1000 m) [59]. Once reaching there, ~0.1% of it gets trapped in sediment eventually becoming source of fossil fuel in the timescale of several million years. It is predicted that if the upper ocean biological pump stops pumping carbon down to the ocean interior, atmospheric levels of CO$_2$ would in time rise by another 200 ppm thereby accelerating global warming further [31].

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Each oceanic region has different significance in influencing the global climate change scenario with their potential for drawing down the atmospheric CO_2 [82]. In this context, the Southern Ocean (SO), being the world's largest high-nutrient low-chlorophyll (HNLC) regions, plays a significant role as a sink for atmospheric CO_2 via its prevailing solubility and biological pumps [20, 100, 102]. Several hypotheses have been proposed to explain the HNLC paradox in SO, among which lack of trace element iron [25] has gathered the maximum attention. Iron plays a key role in nitrogen metabolism of the phytoplankton cell [27] and thus influences carbon fixation efficiency of these microscopic plants. Besides iron scarcity, elevated zooplankton grazing pressure, light, and silicate limitations have also been considered as important factors contributing to low phytoplankton production in the SO [8, 99]. However, the relative importance of the above factors, which may vary with time, location, and local meteorological conditions, in co-limiting phytoplankton bloom events is poorly understood [52].

The role of iron as a phytoplankton growth-limiting factor in the SO was envisaged as early as the 1930s [38]. Though light availability [67] and zooplankton grazing [8] were considered to be the foremost limiting factors of phytoplankton growth, the role of iron as a limiting factor was kicked off after a long gap when John Martin [63] famously stated, "give me a half tanker of iron, and I will give you an ice age," suggesting that the addition of iron might fuel adequate phytoplankton growth resulting in net oceanic uptake of CO_2. Subsequently, several (13) microcosm and mesoscale iron-enrichment experiments were carried out in the world's ocean to test this hypothesis and efficacy of iron experiment. In the SO, seven artificial iron fertilization experiments namely SOIREE (Southern Ocean Iron Release Experiment) [12], EisenEx (Eisen Experiment) [88], SOFeX (Southern Ocean Iron Experiment) north and south [22], SOLAS-SAGE (Surface Ocean Lower Atmosphere Studied-Sea Air Gas Exchange Experiment) [41], EIFEX (European Iron Fertilization Experiment) [90], and LOHAFEX (Loha Fertilization Experiment) [89] have been carried out so far. Besides, two studies, i.e., KEOPS (Kerguelen Ocean Plateau compared Study) [9] and CROZEX (Crozet natural iron bloom and Export Experiment) [77] examined naturally iron-fertilized waters downstream of the SO islands. All these experiments resulted in unequivocal opinion that addition of iron through natural (eolian or volcanic dust) [18, 35, 39] or artificial processes [14, 22] stimulate phytoplankton blooms in HNLC regions like SO [90]. Though there are reports of iron-enriched Patagonian dust reaching the sub-Antarctic Atlantic Ocean through atmospheric corridor [35], comparatively, the flux of iron-enriched dust to the SO is the lowest in the world's oceans [29]. On the other hand, oceanic sources of iron, i.e., upwelling of deep water, vertical diffusion of iron through the water column, re-mineralization of sinking materials, and re-suspension of sediments have been visualized as the probable pathways of iron supply to the surface layers of SO [27, 93].

Despite the HNLC conditions, large accumulations of patchy and spatiotemporally variable phytoplankton biomass (blooms) are frequently observed in surface waters over wide areas of the SO [70, 71, 83, 97], especially where sources of iron are significant, i.e., in the lee of islands [3, 43, 69]. In SO, these blooms play an important role in sequestering atmospheric CO_2 and exporting them to ocean interior through biological pump, enhancing annual biological productivity, and influencing trophic dynamics and biogeochemical cycles of the entire SO [2]. Recent studies by Llort et al. [60] have illustrated how temporal and spatial dynamics of blooms in the SO are more complex than in other oceans, and this complexity is linked to changes in vertical mixing and iron availability. The study revisited the "Critical Depth" theory proposed by Sverdrup [92] and suggested that Sverdrup's blooming conditions are not indicative of the bloom "onset" but of the "climax." Furthermore, they highlighted that the observed bloom complexity in SO is due to the factor (upper layer mixing, and relative depth between mixing layer and the ferricline) that controls different phases (onset, climax, and apex) of the bloom.

Due to global warming, the upper layer of the world ocean is getting warmer, less dense, and thus stratified, which results in lesser nutrients, reduced phytoplankton growth, and diminished pumping to the deep sea [13, 17, 31]. Considering the importance of SO as a sink of the atmospheric CO_2 and the significance of phytoplankton bloom in carbon sequestration especially in HNLC regions like SO, it is necessary to monitor the spatial and temporal distribution of blooms and know their phenology [60, 84]. In situ observations on phytoplankton blooms are sparse around the SO because of adverse weather condition, navigational hazards, remote location, and inhospitable environment with high sea states driven by strong winds [83, 101]. Satellite remote sensing of the ocean color in SO provides synoptic and time-series coverage of near-surface chlorophyll-a concentration (Chl-a) dynamics. The synoptic coverage of Chl-a is widely used to investigate the dynamics of regional oceanographic features such as fronts, eddies, gyres, upwelling zones, plumes, and surface current patterns. Satellite remote sensing took advantage of the fact that all phytoplankton have photosynthetic pigment of Chl-a; therefore, blooms are usually associated with high Chl-a. Since the advent of the Coastal Zone Color Scanner (CZCS), satellite remote sensing is increasingly gaining strength as a very useful tool to study ocean color–related oceanographic features frequently and synoptically. Interesting studies on detection, monitoring, and dynamics of phytoplankton bloom have been made in the past decades using only in situ measurements [15, 27], combining in situ (including moored bio-optical sensors) and remote sensing techniques [1, 33, 49, 83, 84], and modeling approach [52, 68]. Additionally, several iron-enrichment experiments were carried out in SO to test its efficacy in triggering the phytoplankton bloom. Boyd et al. [14] have reviewed the iron fertilization experiments carried out in the world ocean; however, they could not include the results from LOHAFEX (Indo-German collaborative iron experiment in the Atlantic sector of SO), which took place subsequently in the year 2009. The LOHAFEX was designed to cater the next generation of ocean iron experiments specifically targeted to assess the magnitude, depth, and composition of vertical flux in relation to surface productivity and structure of the pelagic food web [89]. To the best of our knowledge, there is no published literature summarizing all the iron-enrichment experiments especially carried out in the SO. In this article, we aim to (i) review the published results from earlier iron-enrichment experiments by artificial and natural sources in the SO, and (ii) quantify the extent of phytoplankton bloom and its evolution using satellite remote sensing observations.

2 Data Analysis and Methodology

Locations of the iron-enrichment experiments and major circumpolar fronts [73] such as sub-tropical front (STF), sub-Antarctic front (SAF), polar front (PF), and southern Antarctic Circumpolar Current front (sACCF) are depicted in Fig. 1. In order to explain the role of sedimentary source of iron for the variability of phytoplankton biomass, Earth Topography One Arc-Minute Global Relief Model (ETOPO1) georeferenced bathymetry data (21,601 by 10,801 cells) has been used to classify the depths shallower than 1000 m (Fig. 2). Northeast shifting of pixel location in ETOPO1 was rectified as the method specified in Jena et al. [45]. In order to characterize the evolution of phytoplankton blooms, Aqua-moderate resolution imaging spectoradiometer (MODIS)–derived Chl-a datasets were acquired from the National Aeronautics and Space Administration (NASA) Goddard Space Flight Center (GSFC). Level-3 climatological (2002–2016) Chl-a composite was generated after discarding the sea-ice and cloudy pixels. Satellite datasets are known to underestimate Chl-a in the SO. Recent analysis by Jena [44] indicated that empirical algorithms used for retrieval of Chl-a from Aqua-MODIS was found to be underestimated by a factor varying from 2 to 2.9. After considering the underestimation tendency of satellite observations, a phytoplankton bloom is defined in this work as the pixels exceeding Chl-a of 0.5 mg/m^3 [43]. Further, monthly composite images from Aqua-MODIS were used to characterize the monthly evolution of phytoplankton blooms (Fig. 2). In order to quantify the contribution of SO blooms to the global ocean, the areal extent of the blooms was calculated for the global ocean and further subset for the SO (Fig. 3). However, the calculated bloom areal extent might have been underestimated from the actual extent considering the spatial gaps of Chl-a retrieval due to cloud coverage. The austral seasons are classified as summer (December to February), autumn (March to May), winter (June to August), and spring (September to November).

3 Artificial Iron Experiments

Out of the 13 artificial iron fertilization experiments carried out so far in the HNLC regions (i.e., $NO_3 > 10$ μM) of the world ocean, 7 in situ experiments were targeted for the cold waters of SO (Table 1) with the first one SOIREE being conducted south of the polar front in austral summer of February 1999. Subsequently, 6 more experiments such as EisenEx (Eisen, i.e., iron in German) in November–December 2000, SOFeX-N and SOFeX-S in January–February 2002, EIFEX in February–March 2004, and SOLAS-SAGE in March–April 2004 and the latest being the LOHAFEX (Loha, i.e., iron in Hindi) January–March 2009 took place in different sectors of the SO involving multinational and cross-disciplinary efforts. The following sections attempt to summarize the significant findings of all the artificial iron-enrichment experiments carried out in the SO.

The SOIREE was a 13 days long trans-disciplinary, multinational experiment performed south of the polar front in Australasian Pacific sector of the SO. Acidified ferrous sulfate ($FeSO_4.7H_2O$) along with an inert tracer sulfur hexafluoride (SF_6) was added to the study site, which has a mixed layer

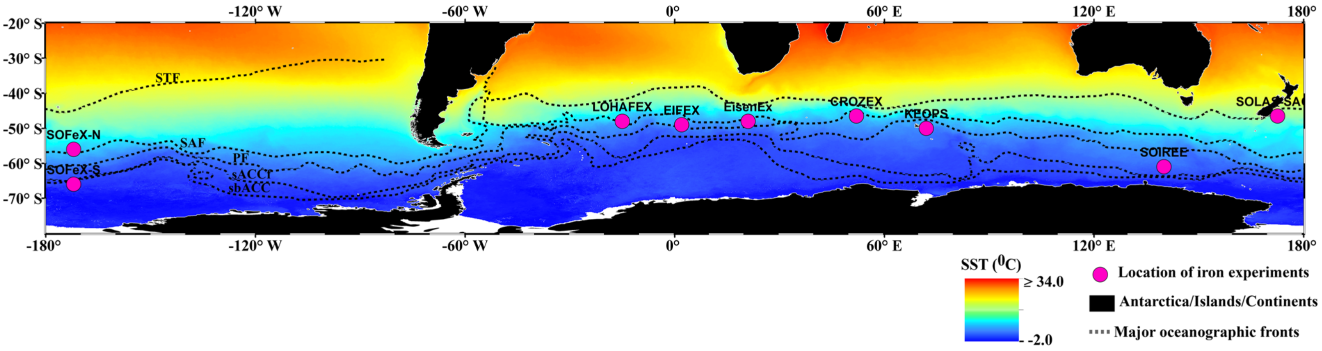

Fig. 1 Study area map showing Aqua-MODIS-derived sea surface temperature (°C) composite during austral summer (2003–2016)

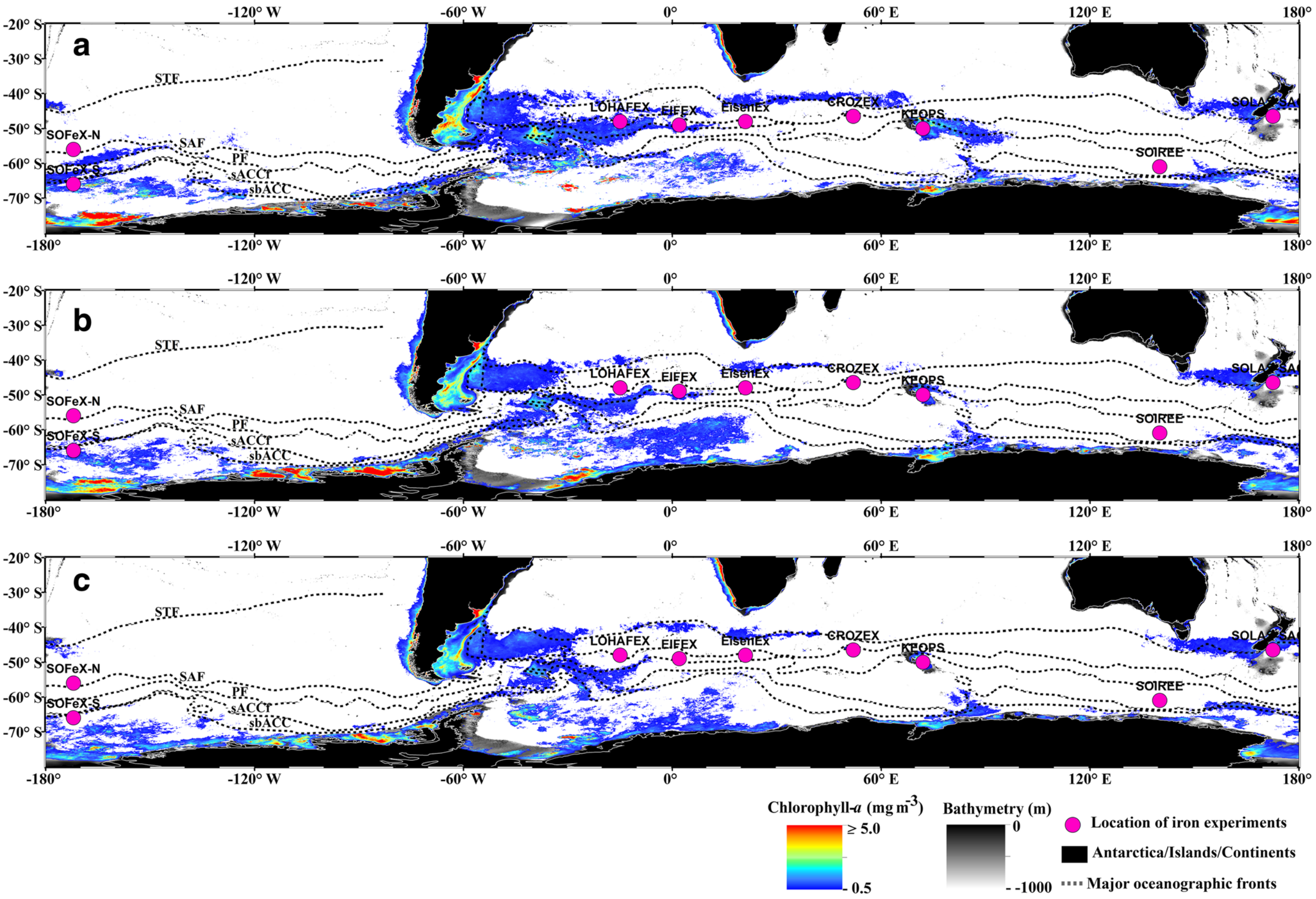

Fig. 2 Aqua-MODIS-derived chlorophyll-a composite (2003–2016) during **a** December, **b** January, and **c** February showing the phytoplankton blooms in the Southern Ocean

depth (MLD) of 65 m [11]. Addition of iron resulted in significant phytoplankton growth and productivity as observed from enhanced Chl-a and production rates, respectively. The bloom patch, which lasted ~ 40 days, could also be monitored using ocean color images from SeaWiFS (Sea-Viewing Wide Field-of-View Sensor). The basis of SOIREE is tightly linked to the findings of IronEx-I and IronEx-II mesoscale experiments carried out in the Equatorial Pacific, which undeniably proved that "iron supply controls algal stocks/productivity." Additionally, the sixfold disparity observed between Chl-a concentrations and associated macronutrient uptake between deck-board and in situ observations in the SO ([25] and

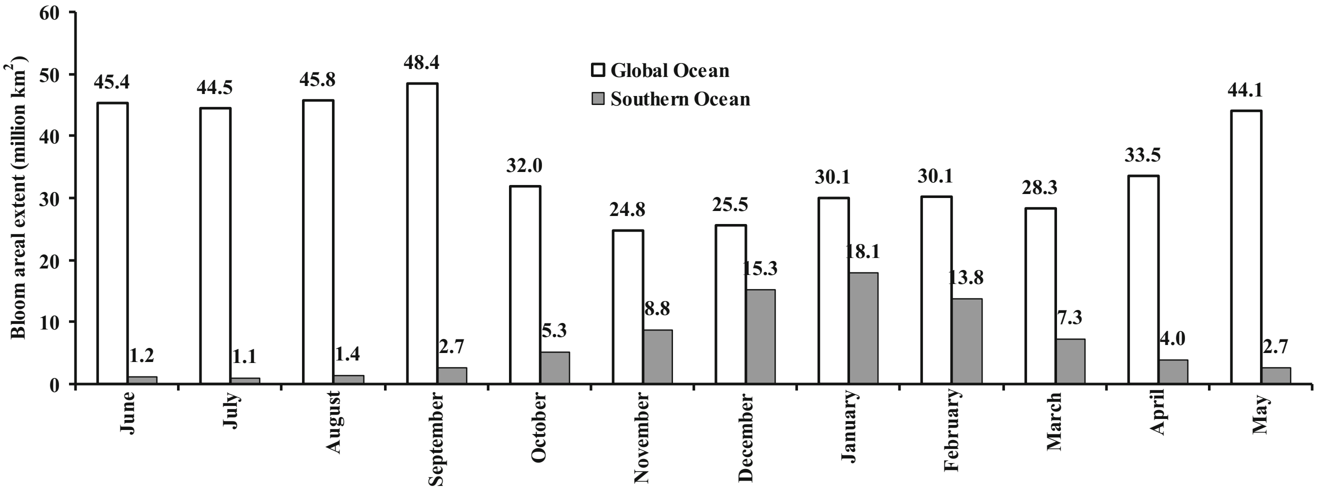

Fig. 3 Monthly areal extent of phytoplankton blooms (pixels exceeding Chl-a of 0.5 mg m^{-3}) in the global ocean and in the Southern Ocean. The SO contributes considerably up to 60% of global ocean phytoplankton blooms during December and January, followed by 45.7% during February

Table 1 General summary of artificial and natural iron–enrichment studies carried out in the Southern Ocean till date

Experiments	Full form	Experiment year	Mode of enrichment	Research vessel	Location
SOIREE	Southern Ocean Iron Release Experiment	1999 (February)	Artificial ($FeSO_4 + SF_6$)	R/V Tangaroa	61° S and 140° E Pacific sector (south of Australia below polar front)
EisenEx	Eisen (i.e., iron in German) Experiment	2000 (November–December)	Artificial ($FeSO_4 + SF_6$)	R/V Polarstern	48° S and 21° E Atlantic Sector (south of polar front)
SOFeX-N	Southern Ocean Iron Experiment	2002 (January–February)	Artificial ($FeSO_4 + SF_6$)	R/V Melville, R/V Revelle, R/V Polar Star	56° S and 172° W Pacific sector (south of New Zealand above polar font)
SOFeX-S	Southern Ocean Iron Experiment	2002 (January–February)	Artificial ($FeSO_4 + SF_6$)	R/V Melville, R/V Revelle, R/V Polar Star	66° S and 172° W Pacific sector (south of New Zealand below polar font)
EIFEX	European Iron Fertilization Experiment	2004 (February–March)	Artificial ($FeSO_4 + SF_6$)	R/V Polarstern	49° S & 2°E Pacific sector (Antarctic polar front: directly south of Africa)
SOLAS-SAGE	Surface Ocean Lower Atmosphere Studied- Sea Air Gas Exchange Experiment	2004 (March–April)	Artificial ($FeSO_4 + SF_6/^3He$)	R/V Tangaroa	46.5° S and 172.5° E Sub-Antarctic waters (south-west Bounty Trough near to New Zealand)
CROZEX	Crozet Islands Experiment	2004–2005 (December–February)	Natural	R/V RRS Discovery	46.5° S and 52° E Indian sector (polar frontal zone near Crozet Islands)
KEOPS	Kerguelen Ocean and Plateau Compared Study	2005 (January–February)	Natural	R/V Marion Dufresne	50° S and 72° E, 51° S and 78° E Indian sector (in and outside of a large bloom off southeast of Kerguelen Islands)
LOHAFEX	Loha (i.e., iron in Hindi) Fertilization Experiment	2009 (January–March)	Artificial ($FeSO_4 + SF_6$)	R/V Polarstern	48° S and 15° W Atlantic sector (sub-Antarctic waters)

references therein) propelled the implementation of SOIREE. Since SO is considered as the source for the intermediate and deep water formation [86], it was chosen for studying iron-induced CO_2 sequestration to the deeper water although it was implicit that such an experiment in polar waters would be logistically challenging [21]. The significant findings of SOIREE are (1) during austral summer, iron limitation of phytoplankton growth was confirmed in SO; (2) from the observed shift in the algal carbon to silicic acid uptake ratio, it is understood that the SO played an important role in the drawdown of atmospheric CO_2 during the last glacial maximum [107]; (3) iron-induced decrease (increase) in pCO_2 (DMS, dimethyl sulfide) levels may exert a negative feedback with respect to future global warming scenario; and (4) the biological response resulting after infusion of iron would largely be influenced by the prevailing physical oceanographic conditions, which not only might allow nutrient-rich waters into the bloom area but also might prevent mass algal sedimentation process by horizontal dispersion of high Chl-a waters out of the bloom area [11].

The SOIREE has demonstrated that intense phytoplankton growth can result after iron limitation is relieved in polar waters; but, it was not clear (i) how the biogeochemical cycling of iron and other nutrients would occur and (ii) what mechanism(s) determines the phytoplankton species dominance in the iron-mediated blooms. Hence, a year after SORIEE, another mesoscale iron experiment named EisenEx [88] took place in the Atlantic sector of SO during austral spring (October–November) of 2000. The 23-day experiment was chosen to be carried out in a cold core Antarctic eddy replenished with higher concentrations of NO_3 and PO_4 but lower SiO_4 concentrations. The EisenEx, also known as CARUSO (Carbon dioxide Uptake Southern Ocean) was led by German researchers in collaboration with other European countries and Japan. All the mesoscale iron fertilization experiments conducted in SO and elsewhere have used $FeSO_4$ as the iron source. During EisenEx, it was confirmed that Fe(II) form is distinctly more soluble than its Fe(III) counterpart, which is thermodynamically stable; however, in warmer waters, the Fe(II) is quickly oxidized to Fe(III) by O_2 and H_2O_2 thereby resulting in overall loss of dissolved iron [66] as observed during IronEx I and II experiments carried out in the Equatorial Pacific. Conversely, in cold waters such as the case in SO, the Fe(II) oxidation rate is significantly slower [23] and thus, it was hypothesized that the Fe(II) might serve as a major proportion of the iron species found in SO. The EisenEx highlighted the spatiotemporal changes in Fe(II) and H_2O_2 (a key oxidant of Fe(II)) and emphasized that, during artificial iron fertilization experiment, the Fe(II) should be allowed to oxidize before acidification, otherwise it might lead to underestimation of dissolved iron [24]. Furthermore, during EisenEx, it was observed that the physical oceanographic conditions (especially the sheer stress) facilitated the bloom patch to spread from 50 to 950 km^2 and storm-induced wind speed have deepened the MLD of the study site from 40 m to 100 m by the end of the experiment [28]. Simultaneously, phytoplankton photochemical efficiency (F_v/F_m), biomass and productivity increased distinctly by end of the experiment and it was found that the growth of different sizes of phytoplankton (i.e., micro, nano, and pico) was controlled by the balance between growth and zooplankton grazing [36]. In addition, the authors observed that the dissolved SiO_4 concentrations did not differ inside from outside of the bloom patch despite there was a significant increase in number of larger diatoms within the patch, which corroborates the fact that iron limitation on diatoms growth and/or diatoms adaptation to low silicate conditions in the SO.

Silicate-dependent, large-sized diatoms play a pivotal role in the export production/biological pump by contributing nearly 75% of the annual PP in the SO [98]. The SO is known for marked variations in silicate concentrations on both sides of the polar front (61° S) with typically low (< 5 μM) and high (> 60 μM) silicate concentrations to the north and south of the PF, respectively [108]. Thus, "silicate availability on either side of the polar front could be a crucial factor for enhancing export production during the iron fertilization experiments." This hypothesis could not be tested during SOIREE and EisenEx since both were performed to the south of the polar front, where silicate concentrations are of intermediate (~ 5–25 μM) levels [36]. Hence, to understand the interaction between silicate availability and iron infusion, two iron addition experiments, i.e., SOFeX-N (span 38 days) and SOFeX-S (span 20 days), were simultaneously implemented during January–February of 2002 by fertilizing two patches (located north and south of the polar front) with sophisticated multi-ship logistics [22]. The MLD at the SOFeX-N site was 45 m deep at the beginning of the experiment gradually deepening up to 55 m after 1 month. SOFeX-N experienced more shear stress than EisenEx due to the presence of several frontal systems in this region [28], and similar to SOIREE and EisenEx, the F_v/F_m, Chl-a, and PP increased significantly from the initial to the final stage [22]. This study reconfirmed that in a Si-limited area, physical oceanographic events such as mixing and dilution process help to maintain low silicate levels inside the bloom patch by entraining dissolved silicate into it (as noticed during SOIREE), thereby facilitating sustained, but silicate-limited diatom production [15, 42]. The silicate-limited production was possible because iron infusion has increased the ability of diatoms to take up ambient low silicate by increasing their maximum uptake rates and lowering half-saturation constants for silicic acid uptake [15]. In other words, interaction between silicate availability and iron infusion can bring in physiological shift in diatoms to overcome Si-limitation by enhancing its ability to exploit low concentrations of silicic acid available in the surrounding waters.

The MLD at SOFeX-S patch remained constant at 35 m and was strongly (60–80%) dominated by diatoms [22]. The increase in F_v/F_m was comparatively higher than that of SOFeX-N, which could be ascribed to the dominance of diatoms. It appeared that, in the early stages of an iron-stimulated bloom, relatively larger diatoms benefit from almost no "grazing pressure" due to absence of abundant specialized grazers (which prefer to feed on large diatoms) to control them when their growth rates are strongly enhanced by the addition of iron [28]. SOFeX-S was conducted in a high-nitrate and high-silicate region and revealed that, after 4 iron infusions, (1) there were no much changes in phytoplankton community structure, but there was a significant shift to intermediate and large-sized cells and more diatoms, which could be quantified from the increased phytoplankton carbon biomass; (2) iron can stimulate export of POC and silica into deeper ocean as observed in the SERIES experiment carried out in northeast Pacific Ocean; (3) though artificial iron fertilization can lead to significant carbon export, it is still modest relative to the carbon export reported during the natural iron-enrichment events in the SO; and (4) extrapolating iron-induced phytoplankton growth to the export production is still to be resolved before geoengineering proposals to mitigate atmospheric CO_2 could be brought into practice [17, 28].

For the first time, results from SOFeX have emphasized that iron fertilization leads to significant export production or enhancement of biological pump in polar waters, which could effectively reduce atmospheric CO_2 levels. To authenticate this, researchers from the Alfred Wegener Institute, Germany, in collaboration with several national and international partners conducted a much longer (39 days) experiment namely EIFEX during February–March 2004 by targeting a 60-km-diameter, vertically coherent (extending to the seafloor at ~ 3700 m), polar frontal cyclonic (clockwise-rotating) eddy in the Atlantic sector of the SO. The goal of EIFEX was to track the fate (growth and decay) of the iron-induced phytoplankton bloom and resolve the influence of the bloom on the carbon budget of the fertilized area [4, 90]. Findings of EIFEX could reveal the potent linkages between SO ecology and regional biogeochemistry. Marked biogeochemical response to iron fertilization could be closely linked to the observed temporal changes in the diatom community structure in the water column. The populations of 45 of the 55 diatom taxa identified during this experiment amplified their abundance inside the bloom patch, implying that artificial iron addition can fuel growth of a broad range of diatom species and their maximum photochemical efficiency [5]. The diatom species that dominated the bloom avoided grazing by zooplankton by either growing fast or evolutionary development of their body armor/frustules, which might be due to the abundant silicic acid available in the SO [10]. The deterrence from heavy frustules restricted the zooplankton grazing to a moderate level (~ 1/3 of the PP inside the bloom patch) during EIFEX [79]. Results corroborated the fact that iron fertilization can lead to transport of organic material to the deep ocean by photosynthetic removal of CO_2. However, the amount of carbon which could potentially be removed by fertilizing the entire SO would account for only a minor fraction of the annual CO_2 emissions globally taking place [4]. One more important point clarified during EIFEX is whether N_2O (atmospheric trace gas with a high global warming potential) formation is triggered by iron addition and that might neutralize the climatic benefits of drawdown of atmospheric CO_2. Walter et al. [106] reported no accumulation of N_2O occurred during EIFEX which is in contrast to the previous report by Law and Ling [56] during SOIREE. They affirmed that iron fertilization does not necessarily produce additional N_2O; moreover, fast sedimentation due to dominance of large diatoms during EIFEX might have prevented the accumulation of N_2O and proposed that N_2O radiative offset should be modeled as a function of not only the production of phytoplankton biomass but also its pathway in the water column.

Although we understand in theory how gases move in and out of the ocean, there have not been many experiments which actually quantified this air–sea exchange, which in turn would facilitate better prediction of the impact of future changes in our climate. Hence, notwithstanding the results of EIFEX regarding the emission of gases with high global warming potential, another 15 days long experiment, i.e., SOLAS-SAGE, with the major aim to study the key drivers influencing the biologically driven exchange of climate-relevant gases (especially CO_2 and DMS) between the ocean and atmosphere were conducted during March–April 2004 in the low-silicate, sub-Antarctic waters (southeast of New Zealand in the vicinity of the Bounty Trough) of the SO. The experiment used the $^3He/SF_6$ dual tracer method to successfully provide a patch-scale air–sea gas exchange estimate in the SO [41, 57]. Two significant results came out of this experiment: first, the influence of strong winds on gas exchange was determined; second, factors controlling the response of phytoplankton after iron addition were clearer. Results indicated that similar to other artificial iron fertilizations, there was a significant increase in the phytoplankton F_v/F_m following iron addition in the first day; however, the biomass and rate of PP has only doubled despite the addition of iron being carried out four times over the experiment [41]. This kind of biological response to the iron infusions was unexpected, which was assumed to be caused by several factors, such as (1) MLD and wind speed was greater than expected leading to strong vertical and horizontal mixing-induced dilution [74], (2) high rate of dilution of the fertilized patch relative to phytoplankton growth rate accounted for 50–65% of loss from the patch center [57], (3) microzooplankton grazing upon the phytoplankton, (4) picoplankton dominated the bloom because lack of silicate, which is required by diatoms for their cell walls, prevented diatom growth, and (5) low light availability. SOLAS-SAGE has clearly established that artificial iron fertilization not necessarily will produce a significant response in all HNLC regions at all times, and in the case of picoplankton-dominated bloom, the iron-induced gain of organic carbon is most likely to be remineralized in the mixed layer rather than sink to the deeper depth [41]. These findings have again raised eyebrows about the efficacy of iron-enrichment experiments as a tool for mitigating global CO_2 emission.

In view of the ongoing controversy regarding future ocean iron fertilization activities, a group of scientists from Germany and India attempted to establish the artificial iron fertilization experiments as a very much part of mainstream modern oceanography by demonstrating its efficacy [89]. For this purpose, the LOHAFEX was carried out in a cyclonic mesoscale eddy at the same latitude with EIFEX in the Atlantic sector of SO during January–March 2009 spanning over 40 days. During the experiment time, the study area was characterized with low-silicate concentration (< 1 μM). The principal aim of LOHAFEX was not much different from other iron fertilization events like SOFeX and EIFEX, which investigated the iron-induced bloom in the surface layer, export production, zooplankton grazing, and bacterial activities. Nevertheless, many interesting findings resulted from LOHAFEX, which have enhanced our understanding about the link between iron addition, response of biological community, and changes in chemical properties in the SO. Analogous to previous report from the other iron fertilization experiments, a diatom bloom was prevented due to co-limitation of iron and silicate. The LOHAFEX has shown that an adequate supply of silicate is a prerequisite for significant, deep carbon sequestration, thereby restricting the region of the SO where significant amounts of atmospheric CO_2 can be sequestered [65]. This finding has certainly cleared the notion that the SO, as a whole, cannot be considered as a sink for atmospheric CO_2. It was observed that addition of iron produced a moderate bloom dominated by pico- and nanoplankton (mostly flagellates) and very less numbers of diatoms. Particle flux study in this very low diatom biomass ($< 10\%$ of the total) patch indicated that waters with low Si:N ratio are not conducive for enhanced POC export even after iron fertilization [64]. Bloom dominated by smaller phytoplankton had a slower sinking rate allowing high grazing activities by copepods. This was closely linked to the observed low downward particle fluxes dominated by copepod fecal pellets with small contribution from larger plankton mostly showing signs of grazing damage. It was assumed that the transparent exopolymer particles (TEP) present in the water column have helped in the aggregation of smaller plankton thereby assisting mesozooplankton grazing upon them [30]. The first-ever study to quantify the role of grazing on promoting iron recycling in this silicate depleted area indicated that strong grazing by copepods during LOHAFEX not only kept the accumulation of phytoplankton biomass in check but also provided regenerated iron through fast recycling of its fecal pellets in the water column. The regenerated iron assisted in sustenance of higher biomass and PP throughout the experiment [50]. LOHAFEX has also highlighted whether iron fertilization has any impact on microbial community or not. Thiele et al. [95] have shown that, although bacterial productivity was enhanced within the bloom, a succession-like response of the microbial community upon the algal bloom was prevented by high grazing pressure, thereby keeping the microbial composition amazingly constant during LOHAFEX. Similarly, the plankton (phytoplankton and zooplankton) diversity also showed remarkable stability throughout the experiment, with no major differences between inside and outside the bloom area, which was presumed to be caused by silicate limitation of diatoms and the absence of salps (a planktonic tunicate) in the fertilized waters. The salps' growth in turn was controlled by abundant presence of the amphipod *Themisto gaudichaudii* (an efficient predator of copepod) in the study area [96]. The observed stability in plankton diversity was in stark contrast to what was reported during the other artificial iron fertilization events.

3.1 Artificial Iron Experiments: Key Questions and Consequences

Mitigation of global warming, by drawing down the atmospheric CO_2, is one of the foremost objectives of the present scientific fraternity. In this connection, various geoengineering schemes have been proposed among which ocean iron fertilization (OIF) is probably the most effective one [89]. Though the short-term OIFs conducted in the world's ocean have been successful to sequester atmospheric CO_2 to the deep ocean and sediments, its feasibility as a long-term option is still debatable considering the fact that there may be potential inadvertent consequences or side effects associated with it, which could eventually pose a threat to the natural marine environment and thus its users [51]. In this section, we recapitulate the future key questions/potential side effects highlighted by earlier studies, which might need attention from the scientific community before regularization of OIF, if planned. The consequences of OIF remain unresolved due to uncertainties in scientific assessment implying that OIF cannot yet be considered as an effective way of carbon removal strategy [14]. Therefore, necessary attempts to evaluate and estimate the pros and cons are highly essential, each time an OIF is contemplated for reducing atmospheric CO_2.

Earlier published literatures [14, 51, 108] have enlisted the probable key questions or potential side effects associated with controlled OIF such as (1) eutrophication followed by enhanced microbial respiration–induced anoxia [86] might occur in the artificially fertilized areas due to differences in circulation patterns, nutrient supply mechanisms, and existing biological communities leading to mass mortality and regime shift in phytoplankton community composition and pelagic ecosystem structure, which afterward may alter the biogeochemical steadiness between iron recycling within, and export from the MLD [14]; (2) OIF is likely to reduce the decreasing trend of pH in the euphotic zone only but its effect in deeper water could be negligible; (3) addition of nutrients will predictably result in redistribution of nutrients on a global scale, i.e., some areas may experience reduction in nutrients supply leading to lower productivity and thus fisheries [51]; (4) photochemical generation of greenhouse gases, other than CO_2, due to eutrophication-induced decrease in O_2 level might trigger the fluxes of climate-related gases such as CH_4, DMS, and N_2O into the atmosphere [7, 55, 58] thereby worsening the global warming scenario; (5) increase in C-fluxes due to OIF may disrupt the benthic ecosystem which is in dynamic equilibrium with the natural C-fluxes (~ 0.4 Gt/year) deposited in it; (6) possible growth of toxic algal blooms [87]; and (7) since the mode of iron supply controls the magnitude, mobilization and retention of bio-available iron (including the C/Fe ratio) in the ocean, it is imperative to take into account the factors influencing the mode of iron supply ([14] and references therein) so as to have a clear picture of the export fluxes expected to generate during any OIF.

4 Natural Iron Enrichment: Physical Forcing and Biological Response

The SO is characterized as the largest HNLC region of the global ocean, with low PP, due to light limitation, lack of micronutrient (i.e., iron), silicic acid concentration, low water temperature, strong grazing pressure, and prevailing physical processes. Despite its HNLC status, development of natural large phytoplankton blooms are frequently observed in the downstream of many SO islands (Kerguelen, Crozet, and South Georgia) due to island mass effect, where the sedimentary source of iron from the island and shallow Plateau fertilizes the mixed layer, resulting in phytoplankton blooms in austral spring and summer when optimum light is available [104]. Various sources (usually five) of bio-available iron to the surface waters of SO have been reported. The iron concentrations in surface waters, far from the Antarctic peninsula, are usually replenished by eolian dust input originating from different continental sources, i.e., from South America (Patagonia) [18], South Africa, New Zealand, and Australia [46] as well as from the iron-enriched deeper waters through the process of upwelling, and vertical mixing, induced by rough bottom topography as in cases of the SO islands [19, 81]. The deep waters in turn are recharged with iron supplied from marine sediments and re-mineralization of particles in the water column [26], and hydrothermal vents located at mid-oceanic ridges [47]. On the other hand, iron in the surface waters of the polar seas are mainly contributed by meltwater from the Antarctic ice sheet [48], entrainment of dirt and resuspended sediments (thus iron) from the grounded icebergs [61], and seasonal sea-ice melting [53].

Phytoplankton blooms in the SO were first reported by Hart [40] and subsequently could effectively be monitored using the satellite remote sensing images [43, 91, 103] because of it synopticity, repetitiveness, and multispectral characteristics. Analysis of Aqua-MODIS data shows that the monthly evolution of phytoplankton bloom areal extent varied from 1.1 to 18.1 million km^2 (Fig. 3). In general, the bloom extent was minimal during the austral winter (1.1 to 1.4 million km^2) and was ascribed to light limitation possibly caused by lower solar elevation angle, cloudiness, and intensive sea-ice coverage. The extent moderately increased during austral spring (2.7 to 8.8 million km^2), reaching at its peak during austral summer (13.8 to 18.1 million km^2), which could be attributed to the conducive environment with the availability of optimum light condition [104], sedimentary source of iron from shallow bathymetric region (< 1 km) that fertilizes the sunlit zone [37], enhanced continental dust advection [18], and supply of iron from the marginal ice zone (MIZ) through sea-ice melting [94] during the austral summer. Subsequently, the extent declined in austral autumn (2.7 to 7.3 million km^2), possibly due to decrease of light availability for phytoplankton growth. The SO contributes nearly 60% of global ocean phytoplankton blooms during December and January (austral summer) (Fig. 3). The dominant region of bloom occurrence is located in the Atlantic sector of the SO, followed by the Pacific and Indian sector of the SO (Fig. 2). The dominant bloom in the Atlantic sector could be ascribed to availability of iron-rich dust input from Patagonia and regional physical processes [35]. The satellite observations provided evidence of phytoplankton blooms resulting from natural sources (mainly in the coastal/shelf waters, downwind of Patagonia and Australia/New Zealand).

In addition, the wind controls the phytoplankton blooms in the SO by mixing the water column, induces upwelling, and modifies the light availability. The variability of Chl-a is known to peak at wind speeds of 5 m/s and generally declines as wind speed increases [33]. The increase in wind speed leads to deepening of mixed layer, thereby decrease in mean light level available for phytoplankton photosynthesis. The proposed mechanism explains the strong inverse relationship between wind speed and bloom occurrence in the SO, because the light-limited phytoplankton in a deeper mixed layer would be less likely to actually bloom, achieving high Chl-a. The role of dust also has a major contribution for the phytoplankton bloom formation in the SO, for example, the widespread observed bloom in the Atlantic sector (Fig. 2) could be ascribed to availability of iron-rich dust input from Patagonia desert [35], in addition to the sedimentary source of iron from the islands and surrounding plateau [104]. The very location of Patagonia desert at the southern end of South America is influenced by the prevailed strong westerly winds, due to the presence of the Andes mountain range. Low-pressure events move northward into the land mass frequently during spring and summer, generating storms with wind speeds exceeding 70 km/h [35]. Moreover, aerosol iron deposition is considered to have first-order control on net community production and export production over the vast areas in the SO [19]. Generally, the dust advection from Patagonia is more frequent during austral summer [34] that leads to the observed blooms condition in the Atlantic sector, as reported in this study.

However, in the absence of any major source of dust input, the sedimentary source of iron from shallow topography or from the islands plays a major role in explaining the observed blooms in the vicinity of the Crozet and Kerguelen Islands and its surrounding plateau. These islands are situated in the polar frontal zone of the SO and are characterized by occurrence of distinct annual phytoplankton bloom in the waters surrounding it. Due to the interplay between sub-Antarctic Front and Agulhas Return Current, HNLC conditions prevail in the south of Crozet Islands [76], whereas north of Crozet often exhibits annual blooms resulting from iron supplied from Crozet [75]. On the other hand, it was reported that the large phytoplankton blooms in the surface waters of Kerguelen Plateau were sustained by the supply of trace element (i.e., iron) and other major nutrients from the deeper layer beneath [9]. The natural iron–enrichment studies carried out during the Crozet natural iron bloom and export experiment (CROZEX) and Kerguelen ocean plateau compared study (KEOPS) demonstrated the role of iron input in modifying the phytoplankton growth. The results from CROZEX experiment in the surrounding waters of the Crozet Islands revealed the north–south gradient in phytoplankton biomass, productivity, community structure [28, 105], and uptake of dissolved inorganic carbon [6] triggered by natural iron fertilization, leading to enhanced particulate organic carbon (POC) flux from sea surface to as deep as 3000 m and ultimately to the ocean floor in spring [77]. The north–south gradient is the effect of iron enrichment throughout the winter (light-limited period) and weak circulation (residence time of water reaching as high as 60 days) in the bloom region [76]. Their study revealed that carbon fluxes from a naturally iron-fertilized productive region of the Crozet Islands were 2–3 times higher compared to the carbon fluxes from an adjacent HNLC region not fertilized by iron. The carbon-export efficiency/carbon-sequestration efficiency (i.e., the ratio of carbon exported to deeper depths to iron added at the surface ocean, C/Fe) during CROZEX (8600 mol mol^{-1}) was comparatively 18 times higher [16] than that of a phytoplankton bloom induced by artificial iron enrichment during the sub-Arctic ecosystem response to iron-–enrichment study (SERIES) in the sub-Arctic Pacific [13]. However, it was 77 times lower than that of another bloom initiated by a natural supply of iron during the KEOPS [9]. Both CROZEX and KEOPS witnessed sequestration of carbon beyond 200 m in the water column. Buesseler and Boyd [16] reported that large losses of artificially added iron (not utilized by phytoplankton) might have led to the lower carbon sequestration efficiency calculated for SERIES phytoplankton bloom, whereas the observed discrepancy in the magnitude of carbon sequestration efficiency between the CROZEX and KEOPS (CROZEX << KEOPS), both naturally enriched, in the SO could be ascribed partly to the underestimation of horizontal iron supply during KEOPS. Considering the vertical, horizontal, and atmospheric fluxes of iron supply, it is presumed that iron supply was higher to the KEOPS bloom prior to the observation started, i.e., the enrichment (through vertical input) could have taken place before stratification of the surface layer during spring or through horizontal input of lithogenic materials from neighboring islands. However, given the methodological differences used to quantify additional iron supply and carbon export efficiency between studies, the exact reason(s) for the broad range of export efficiencies are still not clear ([77] and references therein). Furthermore, the findings from CROZEX highlighted that natural iron fertilization leads to two to three-fold enhancement in new or export production, which could also be corroborated from the carbon flux data recorded at 3000 m and in the sediments beneath this naturally fertilized area than the nearby HNLC region with analogous level of macronutrient concentrations [85] indicating the significance of iron enrichment in influencing the biological pump in the SO.

During KEOPS, two stations, located inside and outside of the phytoplankton bloom, were studied. The study revealed that the bloom was a significant source of CO_2 sink with 2–3 times higher capacity for drawing down partial pressure of CO_2 (pCO_2) than that recorded after iron-addition experiments in SO. The very high estimate of carbon sequestration efficiency (at least 10 times higher than the short-term blooms induced by mesoscale iron-enrichment experiments) observed during this study was ascribed to the longer sustenance of the Kerguelen bloom and its tight coupling with the mode of iron and macronutrients supply through horizontal (from surrounding water) and vertical (from deeper depth) advection rather than atmospheric dust inputs or anthropogenic involvement [9]. Based on the earlier studies in the SO, it was hypothesized that the enrichment of water at deeper depth could result from lithogenic (terrestrial) inputs [54] or by the indirect influence of eolian dust deposition [80]. Results from the KEOPS have emphasized the fact that (i) quantifying the actual amount of CO_2 removed from the atmosphere due to iron (from deep below) fertilization in SO is not straight forward and (ii) the sensitiveness of natural/HNLC region to iron is far more than as inferred from the artificial iron-enrichment experiments carried out in the SO [9]. The results based on the observations made during KEOPS and CROZEX suggest that low grazing pressure and recycled nutrients assisted in the maintenance of phytoplankton blooms [79]. The diatom blooms largely use ammonium, which accounts for 39–77% of nitrogen requirements at Kerguelen Plateau [72] and 67% at Crozet Island [62]. Furthermore, the study has cautioned that the high carbon sequestration efficiency reported during the KEOPS should not be considered as a yardstick for attaining higher carbon sequestration efficiencies through the controversial geoengineering CO_2 mitigation proposals suggested by Chisholm et al. [20] and Buesseler and Boyd [16].

5 Summary

The ocean contains nearly 50 times more carbon than that present in the atmosphere, and we can imagine the critical scenario if major degassing happens. During the pre-industrial period, the SO was considered as a source of CO_2 but with the subsequent rise in CO_2 levels, it is now considered a weak sink of atmospheric CO_2 because of its low productivity. Thus, enhancing productivity by iron fertilization will enhance this sink and increase export of sinking particles to the deep ocean. Usually, the capacity of SO to absorb atmospheric CO_2 varies spatially across the frontal regions. The SO due to its vast stretch of cold water is usually considered as the largest CO_2 sink in the global ocean; areas below 50° S have a major contribution as a CO_2 sink. However, there are reports that the Sub-Antarctic Zone (45 to 48° S) is acting as source of CO_2 due to dissociation of dissolved inorganic carbon in the presence of warm water [78]. Due to the rise in global temperature, it is expected that the degeneration of DIC in warmer oceanic water may accelerate thereby adding more oceanic-CO_2 to the atmosphere. Thus, the entire SO cannot be considered as a CO_2 sink.

Though it is clear that chlorophyll synthesis and nitrate reduction, the two gateways to light and macronutrient usage, respectively, require iron and hence addition of iron can trigger blooms in HNLC waters of the world's ocean enabling drawdown of more CO_2 to the deep ocean, the iron fertilization technique is far from being accepted as a sustainable and pragmatic approach (due to the large ocean area and the limitations associated with the fertilization technique) to meet the challenge of global warming [89]. From different studies, it was confirmed that SO phytoplankton blooms during spring and summer were mainly sustained by iron availability rather than light or zooplankton grazing. Also, the ratio between macronutrients and iron concentration plays a key role in sustenance of blooms (weeks to months) and succession of plankton community structure [14], which is also influenced by the mode of supply of bio-available iron. Despite the fact that all the large-scale iron fertilization experiments carried out so far could not lead to sustainable sequestration of the atmospheric CO_2, the utility and contribution of these shipboard iron experiments to unravel several facts about phytoplankton physiology and carbon dynamics with respect to oceanic processes cannot be overlooked. Thus, more studies on iron experiments with improved experimental design should be carried out, which would provide an ideal platform for researchers to study the dynamics of phytoplankton blooms, which in turn affect the elemental (C, N, S) biogeochemical cycles and ultimately influence the Earth climate system.

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Compliance with Ethical Standards

Conflicts of Interest The authors declare that they have no conflicts of interest.

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