Journal of
Marine Science and Engineering

MDPI

Review

Southern Ocean Iron Limitation of Primary Production between Past Knowledge and Future Projections

Emma Bazzani [1], Chiara Lauritano [2] and Maria Saggiomo [1,*]

[1] Research Infrastructure for Marine Biological Resources Department, Stazione Zoologica Anton Dohrn, Via Acton 55, 80133 Napoli, Italy
[2] Department of Ecosustainable Marine Biotechnology, Stazione Zoologica Anton Dohrn, Via Acton 55, 80133 Napoli, Italy
* Correspondence: m.saggio@szn.it

Abstract: Primary production in the Southern Ocean highly depends on phytoplankton and has been reported to be limited by the availability of the micronutrient iron. The aim of this review is to summarize the past and current knowledge on iron limitation in the Southern Ocean, and specifically how it affects primary producers, thus influencing the whole Southern Ocean community structure, carbon cycling, and large-scale ocean biogeochemistry. In this region, extensive variability exists between different areas regarding iron availability, but also between seasons. Moreover, co-limitations with other abiotic environmental factors exist, further complicating the assessment of the role of iron as limiting factor for phytoplankton productivity. Currently, climate change is altering the Southern Ocean environment. How these changes will affect resident phytoplankton is still not clear, possibly modifying the iron supply mechanisms. Existing projections point towards a possible partial relief of iron stress on phytoplankton, but the interactions between different environmental changes, and the cascade effects they will have, are still poorly understood, and some aspects understudied. Here we try to synthetize the available predictions and uncertainties concerning this topic.

Keywords: iron; Southern Ocean; phytoplankton; climate change; Antarctica; high-nutrient/low-chlorophyll region

check for updates

Citation: Bazzani, E.; Lauritano, C.; Saggiomo, M. Southern Ocean Iron Limitation of Primary Production between Past Knowledge and Future Projections. *J. Mar. Sci. Eng.* **2023**, *11*, 272. https://doi.org/10.3390/jmse11020272

Academic Editor: Sang Heon Lee

Received: 23 December 2022
Revised: 18 January 2023
Accepted: 20 January 2023
Published: 25 January 2023

1. Introduction

The Southern Ocean (SO) includes the largest high-nutrient, low-chlorophyll (HNLC) region in the world. This means that, during the growing season, phytoplankton production does not entirely use the pool of inorganic nutrients available in the euphotic zone, thus leading to a phytoplankton biomass that is lower than expected and relatively high (unused) nutrient concentrations. Jacques et al. [1] referred to this condition in the SO as the Antarctic paradox.

Besides nutrient availability, several variables are known to limit phytoplankton productivity in the SO (i.e., temperature, solar radiation, water stability, and grazing) [2,3], but the role of micronutrients, especially iron (Fe), has gained increasing attention in the past years [4–8]. In fact, even if micro-nutrients are required in small quantities by marine organisms, they are often scarce in the environment and may therefore be limiting for phytoplankton growth. Fe, in particular, is a very abundant element on the planet, but has low solubility in seawater [9]. As a consequence, large portions of the world oceans are subjected to Fe limitation [10]. Considering that Fe-bearing molecules are involved in essential biochemical pathways, including electron transport and nitrate and nitrate reduction, Fe limitation has a great impact on marine organisms. For this reason, Fe scarcity can strongly hinder primary production in marine environments, affecting the global carbon and nitrogen cycles, and hence the large-scale ocean biogeochemistry.

The possibility that low Fe availability may be important for global biogeochemistry was advanced by Martin in 1990 [11]. Today, we have experimental evidence that Fe is present at limiting concentrations throughout most of the SO [12], even if strong geographical (i.e., from coastal areas to open sea) and seasonal heterogeneity exists. Moreover, differences in the distribution of natural productivity and bloom formation have been linked to patterns in dissolved Fe levels [6,13–15], suggesting that Fe availability is in fact a limiting factor for phytoplankton in the SO.

On the other hand, climate change is affecting Fe concentration patterns due to stratification, warming, acidification, and deoxygenation [16]. These changes will strongly influence every aspect of the Fe cycle, including the aqueous chemistry, Fe recycling, sources, and sinks, and ultimately the bioavailability of Fe, thus influencing phytoplankton dynamics, and possibly changing the bases of the so-called paradox.

Naturally, this discrepancy observed in HNLC regions is governed by a combination of physical, biological, and chemical factors, and a single variable is hardly enough to explain it. Here, we focus on Fe limitation as a key factor.

This review offers a brief outline of past SO Fe-related research, which sets the strong foundations on which current experiments and future predictions are based, starting with an overview of why Fe is important and how it is distributed in the SO. Then, we synthesize the current advances in the field, giving key information that serves to contextualize the predictions about how climate changes will affect HNLC dynamics in the SO (i.e., interactions with other environmental factors, influences of Fe availability on community structure, biological plasticity, and adaptations), with a very brief mention of the possibility of using artificial Fe enrichment to mitigate climate change. After looking at how Fe could mitigate climate change, we discuss the current knowledge on how (and if) climate change could actually relieve Fe limitation.

2. Iron in the Southern Ocean

Fe is involved in a diverse range of essential metabolic reactions in marine microorganisms. Most of the cellular Fe is in fact part of important electron transfer proteins involved in the photosynthetic and respiratory pathways, like cytochromes and ferredoxins, but is also present in nitrate, nitrite, and sulfite reductases, antioxidant enzymes, and nitrogenase (Figure 1). Moreover, Fe is important for chlorophyll a synthesis. Thus, it is an essential nutrient for planktonic growth, even if, in vast oceanic areas, including most of the SO, Fe concentrations are very low (<1 nM) [9].

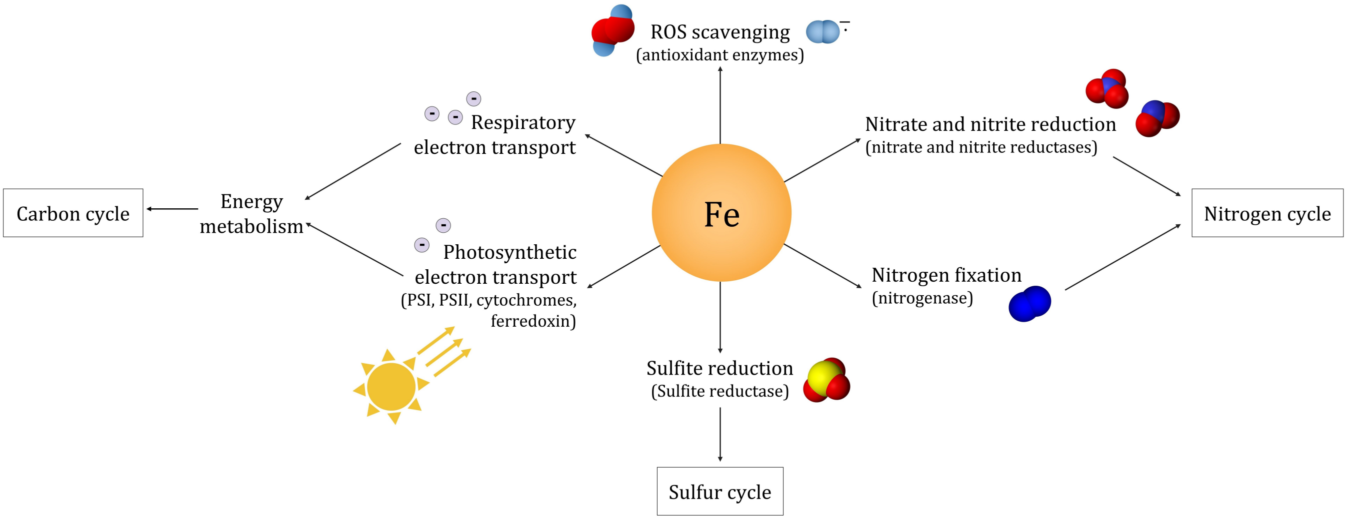

Figure 1. Schematic view of the main processes involving Fe-bearing molecules in marine phytoplankton, and their large-scale impacts on global biogeochemistry.

Biological uptake indubitably accentuates Fe scarcity, but Fe bioavailability in seawater is mostly limited by its chemical speciation. In fact, Fe in water exists in many different forms, free or complexed with organic or inorganic ligands, and in two oxidation states: Fe(II) or Fe(III). Inorganic Fe(II) species are very soluble and only weakly bound when complexed, in contrast to their Fe(III) counterparts [17]. However, the dominant state in oxic seawater is Fe(III), largely unavailable as dissolved, free Fe^{3+}, while species of the more soluble Fe(II) are sporadically present as a result of Fe(III) reduction, which happens by a variety of processes in different environments. In superficial oceanic waters, Fe(III) reduction occurs via biologically mediated reactions at cell surfaces or via absorption of high-visible–low-UV light (photo-reduction) [7]. Either way, the net result of the seawater Fe redox cycling is to increase the concentrations of dissolved Fe(II)′ and Fe(III)′. These dissolved species are the most important Fe sources for phytoplankton [9]. However, dissolved Fe is often not readily bioavailable, because of ligand binding and colloidal particles formation. In fact, dissolved Fe consists mostly of Fe complexed with organic molecules, like organic chelators, humic compounds, or cell lysis products [7]. Organic ligands keep Fe in solution and available for phytoplankton [18], although not in a directly accessible form. Moreover, a variable portion of the dissolved Fe actually consists of small colloidal particles, which are not directly bioavailable [9].

To summarize, Fe uptake by marine microorganisms in the SO is limited not only by its low concentrations, but mainly by its organic chemistry in the oxic, slightly basic conditions that prevail in oceanic waters. Consequently, the combined effects of phytoplankton uptake (and the subsequent downward flux of sinking biomass), particle scavenging, and low solubility limit dissolve Fe to nanomolar concentrations almost everywhere. Specifically, Fe is quickly depleted at the surface [10], where it is more needed by primary producers.

Dissolved Fe concentrations in surface waters are the net result of the combination of dynamic sources, removal, and cycling processes. The supply may occur in many ways, such as Aeolian dust deposition, advection, vertical transport (upwelling from deep waters), biological recycling at the surface, or through river and hydrothermal supply, cryospheric supply (from ice melting), and anthropogenic supply. In the SO, there is a considerable spatial heterogeneity and complexity in Fe distribution and speciation [18]. Here, Fe supply is overly important for productivity, and there is a high variety of Fe sources [19], each one of which can potentially be altered by climate change. Aeolian dust deposition is a major external input for most oceanic waters [10], but little continental dust reaches the SO. In fact, the main sources of Fe here are the continental margins, melting of sea ice and glaciers [20–22], and in large part, advection and upwelling, which are essential for redistributing Fe horizontally and vertically [9,12,23,24]. Many studies agreed that the upwelling Fe flux in the SO strongly prevails over the Aeolian one [12,13,23,25,26]. Specifically, the principal source of Fe in this area is the entrainment of Fe-enriched water during deep winter mixing, increased by the summer upwelling of circumpolar deep waters. However, this phenomenon occurs mainly in autumn and winter, thus a significant part of the upwelled Fe arrives in the surface layer when the conditions are unfavorable for phytoplankton growth [24,25,27], though the summer upwelling can potentially relieve Fe limitation in some regions [28]. Moreover, the cryosphere can affect Fe supply both directly, by releasing the dissolved Fe that is available in the floating ice, and, mostly, indirectly, by affecting the coastal circulation and stimulating advection: sea ice formation and melting leads to deep vertical mixing over the continental shelf, resulting in upward advection or mixing of Fe-rich deep waters [23].

Overall, it is important to emphasize that dissolved Fe concentrations are not uniform. The SO is generally Fe-limited, but it comprises a variety of different environments (bays, ice shelves, sea ice, open waters, polynyas, etc.) and water masses with distinct physical and chemical properties that create heterogeneity in the distribution of dissolved Fe. In general, dissolved Fe increases with proximity to some of the Fe sources, like near the Antarctic coast [29] and in continental shelf waters [6,30]. In these regions, considerable phytoplankton blooms and higher productivity are possible, and have been associated with localized higher dissolved Fe concentrations.

3. Iron Limitation Impact on Primary Production and Ecosystem Structure

If, at present, it is largely recognized that Fe limitation influences the production and fertility of SO ecosystems, it was not until just a few decades ago. The possibility that low Fe availability may influence the large-scale ocean biogeochemistry was first advanced by Martin with the so-called "Fe hypothesis" [11]. Martin's hypothesis actually recalled an old concept that had been neglected for decades, which stated that primary productivity in the SO is limited by Fe deficiency, which leaves major nutrients unexploited. At the time, researchers argued that the persistence of major nutrients at the surface was mainly due to overgrazing of algae by herbivores, the "Grazing hypothesis" [31]. Since then, the relationship between Fe limitation and reduced productivity has been extensively studied [32] and there is now empirical evidence for this association.

3.1. Knowledge from the Past

Prompted by new and more accurate Fe measurement methods, soon after the publication of the "Fe hypothesis", several experiments provided direct observations for Fe limitation of phytoplankton growth in the SO [33–37] (Table 1). Early bottle incubation experiments demonstrated that Fe enrichment resulted in faster nutrient depletion, higher chlorophyll a content, and an increase in net productivity, relative to control samples [33,37–40]. Nevertheless, considering the heterogeneity of the sampling sites (Table 1), clear regional differences started to appear regarding the significance of Fe limitation (see [38]). Also, these studies first suggested that productivity responses and nutrient removal are sometimes accompanied by alterations in the phytoplankton communities and species composition. However, *in vitro* incubations clearly differ from actual ocean conditions and can only give a limited view of the real status of the environment. To overcome the limitations of the small-scale bottle experiments, mesoscale in situ Fe addition experiments were designed, often referred to as "artificial Fe enrichment/fertilization". Between 1993 and 2005, 12 separate field experiments were carried out in which dissolved Fe was injected into different sites of all the known HNLC regions, including the SO (summarized by [41,42]). However, dissolved Fe concentrations dropped rapidly after the initial enrichment unless additional enrichments were performed. Many other Fe fertilization experiments followed (for a detailed review of the fertilization experiments, see [43]). The observed ecosystem responses to Fe addition were strikingly similar in each experiment, and particularly evident in the SO (Figure 2), including: (1) a dramatic increase of phytoplankton biomass and growth rate, (2) improved photosynthetic efficiency (Fv/Fm), (3) increased primary productivity, (4) a large diatom-dominated phytoplankton bloom, appearing after a lag time of some days from the enrichment and accounting for most of the observed increases in production and primary productivity, (5) significant depletion of the major nutrients at the surface, including silicate (Si), and decrease of the surface partial pressure of carbon dioxide ($p\mathrm{CO}_2$).

Therefore, the mesoscale enrichment approach confirmed the important limiting role of Fe for phytoplankton growth and development in the SO, where surface concentrations of macronutrients are high, but Fe concentrations are often limiting. These conclusions have been further validated by the so-called natural Fe fertilization experiments: observations in natural areas where Fe is not limiting and high phytoplankton biomass is observable [37,44–47]. Such areas provide natural laboratories for studying the effects of Fe addition and underlined the fact that a high degree of zonal variability exists in the SO, where localized springtime blooms and elevated productivity are observable along ice edges, near the Antarctic coast, and in some areas of the Antarctic Polar Front, areas where Fe sources are close (i.e., sea ice melting, sediments, and upwelling) [4,13,36,38,48]. Meanwhile, regions lacking close Fe sources have been shown to be the least fertile, despite their high nutrients content [38]. However, additional Si limitation must also be taken into account for some areas [39]. On the other hand, experimental enhancement of dissolved Fe levels can increase phytoplankton biomass and production in coastal waters as well [33], and available macronutrient levels remain above depletion, even if depressed [49–51], suggesting that also Antarctic shelf water communities can be Fe-limited.

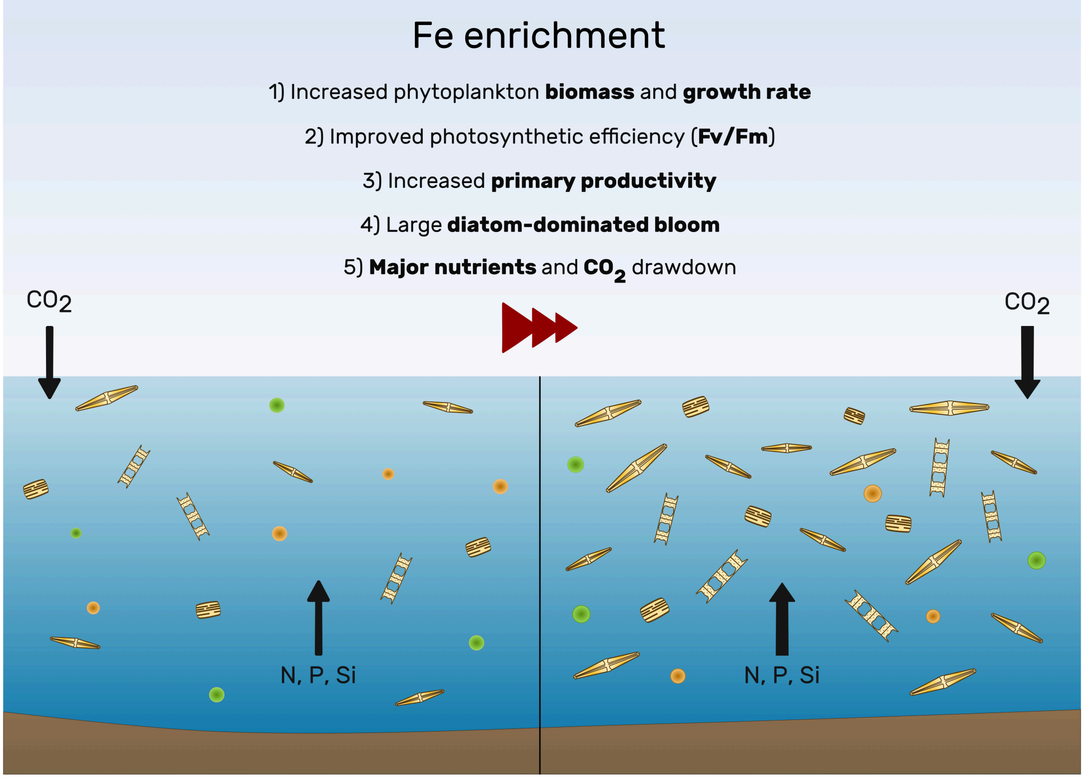

Figure 2. Main effects of artificial Fe enrichment experiments. Abbreviations: Fe stands for iron, CO_2 for carbon dioxide, N for nitrogen, P for phosphorous, Si for silicates, Fv/Fm indicates photosynthetic efficiency.

Table 1. This table summarizes the main experiments conducted to test the Fe hypothesis and how Fe concentration impacts phytoplankton growth. Emphasis is on the variety of sampling sites and periods. Abbreviations: SOIREE stands for SO Iron Release Experiment; in EisenEx, "Eisen" means Fe in German; SOFeX-N,S for SO Fe experiment North and South; EIFEX for SO European Iron Fertilization Experiment; SAGE for Surface Ocean–Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange; in LOHAFEX, "Loha" means Fe in Hindi; CROZEX for CROZet natural iron bloom and EXport experiment; KEOPS 1,2 for Kerguelen Ocean and Plateau compared Study.

Experiment Type	Area	Period	Reference(s)
Artificial Fe fertilization	SO Australian Sector	Summer (Feb)	SOIREE [52–54]
	SO Atlantic Sector	Spring (Nov)	EisenEx [55]
	Polar waters of New Zealand, north of the Polar Front	Summer (Jan–Feb)	SOFeX-N [56]
	Subpolar waters of New Zealand, south of the Polar Front	Summer (Jan–Feb)	SOFeX-S [56,57]
	SO Atlantic Sector	Summer–Autumn (Jan–Mar)	EIFEX [58]
	Subpolar waters of New Zealand	Autumn (Mar–Apr)	SAGE [59]
	SO Australian Sector	Summer–Autumn (Jan–Mar)	LOHAFEX [60,61]
Natural Fe fertilization	SO Atlantic Sector	Spring (Oct–Nov)	[13]
	SO Pacific Sector	Autumn (Mar–Apr)	[36]
	Crozet Plateau	Spring–Summer (Nov–Jan)	CROZEX [37,47,62]
	Kerguelen Plateau	Summer (Jan–Feb)	KEOPS 1 [45,46]
	SO Pacific Sector	Summer (Jan–Feb)	[30]
	Kerguelen Plateau	Spring (Oct–Nov)	KEOPS 2 [63]

Table 1. *Cont.*

Experiment Type	Area	Period	Reference(s)
In vitro Fe enrichment (bottle incubation experiments)	Weddel Sea; Scotia Sea	Spring–Summer (Nov–Dec)	[33]
	SO Pacific Sector	Autumn (Mar–May)	[39]
	Subantarctic Zone (SE New Zealand)	Autumn (Apr–May) Spring (Oct–Nov)	[64]
	Polar Frontal Zone, Pacific Sector	Spring (Oct–Nov) Summer (Jan–Feb)	[65]
	Subantarctic Zone, Australian Sector	Late Summer (Mar)	[66]
	Subantarctic Zone, Australian Sector	Late Summer (Mar)	[67]
	Ross Sea	Summer (Jan)	[38]
	Antarctic Circumpolar Current	Spring–Summer (Oct–Dec)	
	Polar Frontal Zone, Atlantic Sector	Summer (Dec–Jan)	[40]
	Crozet Plateau (Polar Frontal Zone)	Spring–Summer (Nov–Jan)	[37,47]
	Amundsen Sea	Summer (Jan–Feb)	[49]
	Scotia Sea	Spring (Oct–Dec) Summer (Dec–Feb)	[68]
	Amundsen Sea	Early summer (Dec–Jan)	[69]
	Ross Sea	Summer (Dec–Feb)	[70]
	Subantarctic Zone, Atlantic Sector	Summer (Dec–Feb)	[15]
	Polar Frontal Zone (North);Antarctic Zone (South), Atlantic Sector	Summer (Dec–Feb)	[71]
	Ross Sea	Early Summer (Dec–Jan)	[72]
	East Antarctica	Late Summer (Jan–Mar)	[73]

Satellite observations have confirmed the presence of natural phytoplankton blooms stimulated by different Fe inputs [48], and computational analyses with ocean models have confirmed that not only primary production, but also community structure and the sinking flux, can be influenced by variations in the Fe sources [74]. These experiments paved the way for the next decades of Fe studies and were essential to confirm the importance of Fe in the SO, which was previously only hypothesized.

3.2. Co-Limitations with Other Environmental Factors

The polar nature of the SO presents important challenges to primary producers, which must live under growth-limiting concentrations of Fe, but also under extreme light and temperature conditions. Moreover, among the major nutrients, Si can be strongly limiting for diatom growth and thus influence productivity. On the other hand, Si concentrations are seldom limiting in nutrient-rich SO waters [75]. More recent studies have further confirmed the positive effects of Fe addition on phytoplankton growth and photosynthetic efficiency in Fe-limited areas of the Scotia Sea [68], Amundsen Sea [69], summertime Ross Sea [70], and the Sub-Antarctic zone [15], but they also pointed out how irradiance might limit phytoplankton production as well [71–73].

3.2.1. Light

Being that light is a main driver of photosynthesis, the issue of light limitation has always been studied, especially in the SO [37,47,48,64,66,76], where the polar darkness prevails for much of the year and all other variables are merely additive during darker periods. However, even during the Antarctic summer, light can be somewhat limiting, due to the low angle of incidence of the sun rays, or where the mixed layer is deep and turbulent and draws the algae down into the dimly lit part of the euphotic zone [2]. Moreover, for oceanic phytoplankton, an antagonistic relationship exists between cellular

Fe and light-harvesting capacity, owing to a higher demand for photosynthetic Fe-based redox proteins by low-light-acclimatized algae, causing the negative effects of the two factors to reinforce one another [76]. Accordingly, some of the recent studies on Fe and light co-limitation showed that Fe addition can boost phytoplankton growth, but only when sufficient light is available [73], pointing towards irradiance as the main limiting factor. However, spatial [71], taxonomic [47], and of course seasonal variability exist for the relative importance of Fe and light limitation. Moreover, studies on laboratory-cultured [77] and natural [72] phytoplankton populations have suggested that SO species evolved Fe-saving strategies to cope with low light levels, partially relieving the additive effect of the two factors [78]. Specifically, both diatoms and the Antarctic bloom-forming haptophyte *Phaeocystis antarctica* showed increased size of photosynthetic units under low light irradiances, instead of increased numbers of units [77]. This strategy allowed them to reduce the Fe burden of photosynthesis, and their Fe requirements decreased or remained relatively constant with decreasing light, in contrast with temperate diatoms [77]. Moreover, Ryan-Keogh et al. [70] found that phytoplankton species that utilize this Fe-saving strategy were favored in the Ross Sea late-summer season, which may explain the typical seasonal transition in bloom-dominating species observed in this region. Interestingly, most, but not all, diatom species show an additive effect of Fe and light stress [78]. For example, some species (i.e., *Chaetoceros* cf. *sociales*, *Pseudonitzschia subcurvata*, *Actinocyclus actinochilus*, and *Navicula* sp.) showed a similar reduction in the growth rate when subjected to Fe and light reduction, or a combination of the two, suggesting that an additive relationship does not exist in these diatoms. In contrast, an additive effect was observed in some polar diatoms, like *Fragilariopsis cylindrus*, *Thalassiosira antarctica*, and *Proboscia alata* [78]. This, of course, is not the only Fe-saving adaptation that SO phytoplankton uses to overcome limiting environmental conditions and maintain photosynthetic efficiencies and production rates. Additional strategies include lower respiration rates, the use of proteorhodopsins, Fe-free proteins which may allow the production of additional ATP, and the replacement of the Fe-containing photosynthetic proteins, i.e., cytochrome c6 and ferredoxin, with the copper protein plastocyanin or the nonmetal protein flavodoxin, respectively, under Fe limitation. Fe-saving strategies have been studied mainly in diatoms and are discussed by Strzepek et al. [79] and Coale et al. [80].

3.2.2. Temperature

Temperature is the other environmental factor that should be considered prohibitive for phytoplankton to thrive in the SO. Temperature increments, for example, even if to a lesser extent, have been shown to have a possible synergistic effect with Fe on Antarctic phytoplankton [81–83]. Bloom-forming *Pseudonitzschia* species from the Ross Sea showed significantly increased growth and high managing capabilities for cellular Fe demand under warmer low-Fe conditions [83]. Nevertheless, SO phytoplankton species are notably adapted to the characteristic low temperatures of their natural environment, and not all of them are affected by a temperature increase in the same way [82,83]. Some studies have also suggested that low temperatures may actually have a role in facilitating the aforementioned increased light-harvesting antenna size adaptation [79]. In fact, large antennae are usually disadvantageous because they potentially increase energy loss as heat and fluorescence, but heat loss should decrease with lower temperatures [79].

3.2.3. Silicates

As already mentioned, Si concentrations are usually not limiting for phytoplankton growth in the SO. However, in some areas, like the Subantarctic zone north of the Polar Front [67], they can exert significant control on the growth of some species of phytoplankton, primarily diatoms [36,64], which use silicic acid ($Si(OH)_4$) as a structural component of their cell walls. Many observations point out that phytoplankton communities north and south of the Antarctic Polar Front respond differently to Fe addition [56,65], because natural concentrations of $Si(OH)_4$ limit diatom productivity in the north, especially in the late growing season. In fact, the community composition here tends to shift towards larger, non-siliceous cells, or small diatoms, in response to Fe addition [47,56,65]. Nevertheless, field studies suggest that Si frequently acts only as a secondary limiting nutrient compared to Fe [15,56,67,74].

This section highlights how it is hardly possible to trace back the (apparently) paradoxical situation in the SO to one cause or variable, except at small scales. Even if the role of Fe is now established to be crucial, it is unlikely that Fe alone limits phytoplankton production. Rather, it appears that: (I) there is a primary productivity pattern synchronized with seasonal irradiance, (II) the Fe supply primarily controls phytoplankton growth during late spring and summer, except when (III) Si limitation is strong and constrains diatom blooms [27,75]. Thus, primary productivity in the SO is restricted due to Fe deficiency, in combination with severe seasonal effects of irradiance and wind mixing (which affects the light climate), as well as regional Si limitation for diatoms. Fe distribution, hence, plays a critical role in determining the development of phytoplankton blooms during the growing season, thus regulating primary production, with effects on the whole SO community structure.

3.3. Phytoplankton Community and Ecosystem Structure

In general, it has been shown that small cells are favored under Fe limitation due to higher surface-to-volume ratios that facilitate Fe uptake by diffusion [76]. Moreover, small algae predominantly rely on recycled ammonium as nitrogen (N) source, and thus have a lower Fe requirement, as it is needed for nitrate and nitrite reduction [9,12].

In the SO, there is geographical and seasonal variability in the proportions of the phytoplankton size categories, but generally the biomass is dominated by nanoplankton and picoplankton [2,34,39,84], while the contribution of larger phytoplankton species is limited. Diatoms and *P. antarctica* typically dominate phytoplankton groups in Antarctic waters, and diatoms in particular appear to be especially limited by low Fe in this region [12,15,58]. Fe availability highly influences phytoplankton species composition. A case study is offered by offshore waters of the Ross Sea, where in recent years changes in the abundance of phytoplankton have been recorded during austral summer [85,86]. Here, the ice-free areas were usually HNLC because of Fe limitation of phytoplankton growth [87], but recently, considerable biomass increase and large-sized phytoplankton were observed [85,86,88], suggesting relevant alterations in Ross Sea summer productivity. During these observations, the phytoplankton of the ice-free Ross Sea showed significant anomalies. For example, *P. antarctica* colonial bloom occurred in an area and in a season usually characterized by the prevalence of diatoms. Conversely, diatoms dominated the wide upper mixer layer. These changes are thought to be driven by modifications in the circumpolar deep-water circulation [89,90] and variations in the benthic sources which supply Fe to the system [88]. However, it is unclear what main environmental factors are driving these changes in primary production and the prevalence of different functional groups [91,92]. The current asset may affect not only the Ross Sea, but the entire SO ecology, also having an impact on a global scale.

Several other studies have indeed demonstrated that Fe limitation and Fe enrichment affect the phytoplankton species composition, even though there is some intrinsic variability in the results, which is mainly due to the natural heterogeneity of the starting communities utilized for the experiments, which differ between sampling sites and periods. However, a commonly reported result is a general increase in larger size categories. Hinz et al. [68], for example, observed significant differences in the phytoplankton community structure after Fe addition, but only in the samples collected from naturally Fe-limited areas or from a naturally Fe-fertilized area at the end of the growing season. Specifically, a general increase in medium and large diatoms was observed in these regions, suggesting that these groups were in fact Fe-limited. These results are in agreement with the before-mentioned results from mesoscale Fe addition experiments, which prompted strong growth of larger microphytoplankton species, especially diatoms [42,55,58], and in line with the outcomes of many other bottle incubation experiments following Fe addition [40,47,64,68,73]. Moreover, cell numbers of medium and large-size diatoms increased during observation of naturally Fe-limited regions with episodic Fe-driven diatom blooms [13,27,36,42]. The success of larger diatoms is consistent with the idea that medium and large diatoms have higher Fe requirements, while being less susceptible to grazing, thus particularly favored when Fe limitation is relieved, assuming that the region is not Si-depleted. In fact, no taxonomic shift toward diatom-dominated communities was observed during experiments conducted in Si-limited regions, such as SAGE and LOHAFEX (Table 1) [59,60], but was present during SOFeX-N [56]. On the other hand, some medium-small diatoms, including but not limited to *Cylindrotheca* spp. [68] and *Pseudonitzschia* spp. [40,47,55,56,68], also showed increased biomass in Fe treatments, demonstrating that small phytoplankton species exhibit a Fe response as well, besides having lower Si demands [67]. Notably, both small and medium-sized *Pseudonitzschia* spp. responded in different regions of the SO. A recent study also found that *Pseudonitzschia* spp. can up-regulate Fe-conserving photosynthetic processes, use low-Fe nitrogen assimilation mechanisms, and increase Fe uptake and storage during Fe limitation, indicating that this genus may have great impact on SO production and carbon export [83].

In general, it can be concluded that, in the SO, the Fe-enriched community often tends to a shift towards a diatom-dominated community [15,58,70], being diatoms the main beneficiaries of Fe addition. This shift is suggestive of community-specific Fe quota requirements [77], which guide the composition of the existent phytoplankton community in the SO. Oceanic single-celled algae are the basis of the ocean food web, and the whole community structure is influenced by phytoplankton species composition [50,93]. For instance, *P. antarctica* can form large colonies at high Fe concentrations [94], which influence its susceptibility to grazing. Similarly, large diatoms are too big to be easily grazed by microzooplankton grazers. As larger mesozooplankton grazers normally have lower growth responses [42], this allows bigger blooms to form, with cascade effects on higher trophic levels, major nutrients and carbon drawdown, and biogeochemical ramifications on local and global scales.

3.4. Where We Are Today: Artificial Fe Fertilization and Carbon Export

Thanks to the research conducted in the past three decades, Fe has now been established as a key resource that influences the magnitude and dynamics of primary production in the global ocean, thus shaping CO_2 fixation and the whole carbon cycle. As a consequence, the carbon export by the biological pump is presently limited by the insufficient Fe availability [11]. Oceanic waters, in fact, can store carbon on decal to millennial timescales, thus regulating the atmospheric pCO_2 with effects on the global climate. According to the Fe hypothesis, atmospheric Fe supply to the SO during the last glacial maximum enhanced biological productivity, and the corresponding atmospheric CO_2 drawdown [11]. Decades later, the idea that Fe fertilization can change the global climate through the reduction of atmospheric CO_2 has been confirmed [95]. Meanwhile, this assumption inspired research on the use of Fe fertilization to stimulate oceanic carbon sequestration through the biological pump in Fe-limited regions and mitigate future climate change [26,96,97]. The past in situ Fe fertilization experiments were specifically designed to test the Fe hypothesis and showed indeed higher CO_2 uptake and increased particulate organic carbon (POC) concentrations in the surface layer, as a response to Fe addition (details are summarized in [43]). However, an increase in the carbon export flux from the surface layer (i.e., the magnitude of Fe-induced carbon export below the winter mixed-layer depth) was much more difficult to prove [26,42]. The only exception was the SO, where the Fe-induced carbon export exhibited a small but significant increase during some long-term monitoring experiments [56]. Later, with the EIFEX project, which was performed within the core of an eddy, researchers were able to prove and to measure long-term carbon sequestration in ocean bottom waters and sediments following Fe-fertilized diatom blooms [98]. However, these ocean fertilization experiments are still debated because of their ambiguous relevance, mostly in terms of carbon sequestration [41,57,99], and in recent years similar Fe fertilization experiments have rarely been performed. Nevertheless, they allowed to better understand of the functioning of plankton-based ecosystems and some HNLC dynamics [96], while also highlighting the necessity of methodological improvements, including better selection of the study sites (i.e., sites without additional influences such as Si and grazing pressure), longer monitoring periods, the implementation of new techniques for more reliable measurements and quantifications, and the evaluation of potential dangerous side effects on the system [43]. Today, Fe fertilization is among the possible carbon drawdown strategies discussed by the Intergovernmental Panel on Climate Change (IPCC) [100]. However, other studies are more cautious, and the IPCC itself also underlined a range of uncertainties and open questions about the feasibility and the large-scale consequences of Fe fertilization [100–102]. Moreover, a simulated glacial Fe fertilization pointed out that additional processes might have been significant contributors to the past decrease in the glacial CO_2 [103], and the complexity and diversity of the drivers of ocean carbon sequestration (besides the biological sinking pump) is still emerging [104]. Thus, while the connection between Fe limitation and primary productivity is now established, direct evidence of its precise impact on carbon export is still lacking [105]. Moreover, potential side effects have emerged as harmful consequences of Fe enrichment [106], such as negative climate and ecosystem changes [97,106,107], due to the possible production of climate-relevant gases (e.g., nitrous oxide, N_2O; dimethylsulfide, DMS; and methane, CH_4) [97,106,107], or the development of suboxic/anoxic conditions in the water column [97,106,107] and toxic algal blooms [108,109], thus sparking the debate between those who support and those who oppose artificial ocean Fe fertilization experimentation. Overall, the progressively decreasing magnitude of CO_2 sequestration over time during the experiments, the monitoring difficulties, the possible negative side effects, and the many uncertainties must be thoroughly addressed and modelled before making any attempt of Fe fertilization at large scales for climate mitigation. As the matter of Fe-stimulated carbon export is still currently debated, it is only possible to speculate. Surely, Fe enrichment played a role during past glacial eras, but the recreation of such conditions through artificial fertilization cannot currently be proved.

4. Looking to The Future: Could Climate Change Relieve Iron Limitation?

The Fe cycle comprises diverse processes: external supply, chemical speciation, transformations, biological uptake, recycling, and the removal by sinking particles. Each one of these processes is, and will be, affected by the changes that the global oceans are experiencing [100], likely at different magnitudes and with potential cumulative effects, which complicate possible predictions. Timing, direction, and scale of climate change impacts in the Antarctic region differ sub-regionally [100,110]. Moreover, future climate changes will strongly influence phytoplankton dynamics themselves, and the biological Fe demand will vary due to acclimation and adaptive evolution to environmental changes. Thus, to make predictions about modifications in phytoplankton communities and productivity in the next centuries, it is essential to understand the positive and negative feedback interactions of Fe biogeochemistry with the changing oceans and the biology of the organisms involved. To date, accurate modeling and projections of future Fe cycle and its impact on SO productivity require further advances in both data collection and conceptual understanding. Nevertheless, it is apparent that there will be shifts in Fe biogeochemistry, from cellular physiology to global-scale oceanic circulation (as summarized in Figure 3).

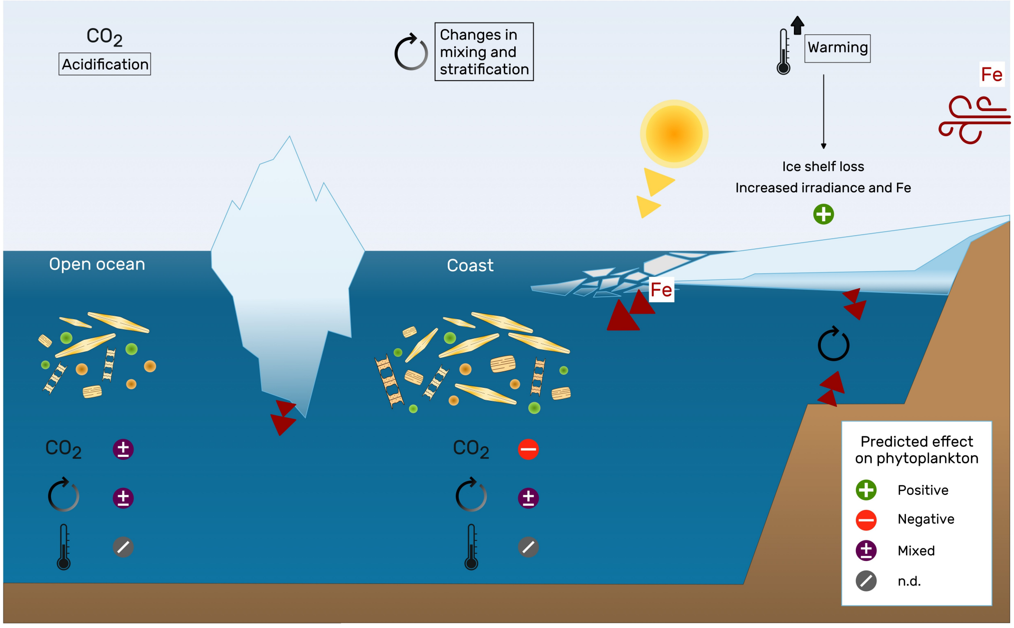

Figure 3. Schematic representation of the predicted effects of anthropogenic climate change on the SO phytoplankton community through three main climate-driven processes: acidification, stratification, and warming, according to the data summarized in the 2019 and 2022 IPCC reports [100,111], and as discussed in the text (Section 4.2). The figure also shows the possible changes in cryosphere dynamics and their consequences on the Fe supply, as a general overview. The complexity and the details of the subject are discussed in the text (Section 4.1). In general, the future effects of acidification, as the ones of modified stratification, could be positive and negative at the same time, while the consequences of increased temperatures are still not defined for phytoplankton due to high variability in the results. However, warming is expected to have a positive indirect effect on future phytoplankton, thanks to the resulting increase in ice melting rates and consequent Fe release and reduced ice cover. More details on the confidence levels of these predictions can be found in the 2019 IPCC report on polar regions [111].

4.1. Iron Supply

In the SO, Fe supply is extremely important for productivity and CO_2 drawdown [95], and relies on numerous and different Fe sources, most of which will be affected by climate change. Cryosphere dynamics are probably the most influential and highly studied research topic regarding future climate change in the SO. How will changes in cryosphere dynamics influence Fe supply to SO waters in the future?

Already in the 90s, the importance of drifting "dirty" icebergs was discussed as an important Fe source for the Fe budget in some productive regions [33]. Loss of ice and glacial mass has been predicted with very high confidence for polar regions in the future [100]. The potential to directly release dissolved and sediment-bound nutrients to the surface ocean, and to indirectly stimulate nutrient upwelling is expected with ice melting [100]. Thus, ice shelves and glacial melt may become increasingly important Fe sources in some SO regions, due to anthropogenic warming [21,30,112–114], while drifting icebergs have the potential to fertilize the SO far from the coastal waters [20,115].

Climate-change-driven community shifts have already been observed in ice-free Ross Sea areas [85], as mentioned in Section 3.2. The calving of the Mertz Glacier Tongue in 2010 altered the surrounding ecosystem, causing a meltwater-induced diatom bloom due to increased light and Fe, which doubled the seasonal uptake of carbon [112]. Thus, glacier retreat could potentially increase the release of Fe-rich material from shallow suboxic shelf sediments, a source that may become increasingly significant for the local Fe supply, also because of the potential cutting out of deep water supply due to increased stratification [114]. Moreover, ice shelves retreat can potentially bring to the formation of new polynyas in their wake, or to increased productivity of pre-existing polynyas [111]. Given the amount of residual macronutrients in surface waters, polynya productivity has the potential to increase due to future changes in ice melt rates [30], with influences on whole coastal ecosystems and an enhanced capacity of Antarctic continental shelf waters to sequester atmospheric CO_2 [116]. The collapse of the Larsen A and B ice shelves in the Antarctic Peninsula offered a case study to observe the effects of ice shelf disintegration. The Larsen embayments function now as new high productivity areas, with probable ramifications for organic matter export and the evolution of the whole marine ecosystem [113].

Finally, with glacier retreat, ice-free land areas are likely to enlarge, causing a possible enhancement of the Fe flux to sea ice via dust deposition [117]. On the other hand, some argue that the current rate of glacier retreat may end up in total loss of glacial cover, and consequently stop the glacial Fe supply to coastal waters. Thus, the link between the continental sources and the offshore surface ocean would be cut, with a high impact on some of the most productive regions in the SO [22,118].

It is important to note that warming-driven changes in the cryosphere will not only affect ice-born Fe supply, but will influence most Fe sources by changing the water circulation (i.e., causing mixing and upward advection) [23], by increasing stratification due to changes in the wind fields [113], and by potentially stimulating Aeolian dust deposition (i.e., with the expansion of ice-free land areas) [117]. This interdependence of different Fe supplies highlights the vulnerability of coastal Antarctic ecosystems to changes in ice basal melt rates. Moreover, besides the influence on Fe supplies, climate change will also affect other factors that are important for Fe bioavailability to phytoplankton, mainly the chemical speciation [16]. However, many aspects of the ocean Fe cycle are currently understudied, and more research is needed to better predict future changes in chemical speciation, abiotic removal and scavenging, and their effects on Fe bioavailability. On the other hand, we have a better understanding of phytoplankton physiological and community-level responses to changes in the Fe supply.

4.2. How Will Changes in the Environment and Iron Cycle Affect Phytoplankton Biology?

4.2.1. Warming

As already mentioned, Fe addition and warming together often show stimulatory and interactive effects on Antarctic diatoms [81,82,119]. Moreover, warming and Fe have been found to be the most influential climate change factors in a multivariate analysis considering the effects of multiple variables on a model diatom from the genus *Pseudonitzschia* [120]. Interestingly, experimental evidence has shown that warming alone could not only stimulate considerable growth and nutrient drawdown, but also compensate for Fe limitation, and maybe even improve Fe-use efficiencies, although this is not true for all diatom species [16]. Even dominant diatom groups exhibit important molecular and physiological differences [83]. In particular, the genus *Pseudonitzschia* has shown resilience and enhanced growth and nutrient drawdown with rising temperatures, even under low-Fe conditions, which suggests an increasingly important role of this genus in warming SO ecosystems [83]. However, overall, ocean warming is expected to put pressure on Antarctic phytoplankton and favor the spread of invasive species [100].

4.2.2. Acidification

Acidification, like warming, is another primary global change phenomenon, derived from increased CO_2 levels. Acidification may influence Fe aqueous speciation [16] and consequently Fe availability, but it can also potentially affect phytoplankton community structure and Fe demand with both direct and indirect effects. Calcifying phytoplankton species will probably be affected in different, often opposing ways, i.e., showing decreased calcification due to acidification, while exhibiting higher photosynthetic rates due to increased CO_2 levels [100].

Incubation experiments with Antarctic HNLC communities often show that the effects of changing CO_2 are secondary to the relief of Fe stress [121,122]. Nonetheless, it should be mentioned that in most experiments, Fe addition exceeded the proposed Fe levels in model projections, while acidification treatments typically mimic predictions more accurately [16]. Furthermore, CO_2-mediated shifts in diatom community structure have been reported [121,122], and a critical threshold for tolerance to ocean acidification has been identified in a coastal phytoplankton community [123]. CO_2 concentrations over the threshold negatively affected photosynthetic performances and primary productivity, and consequently reduced nutrient uptake, chlorophyll a accumulation, and particulate organic matter (POM) production [123]. Species-specific variability exists regarding growth and primary production responses to acidification.

4.2.3. Mixing and Stratification

Changes in stratification will affect mixed-layer depths, a leading regulator of primary production. Deeper mixed layers bring more nutrients to the surface; however, they also result in lower irradiance levels available for phytoplankton growth. Model projections suggest that there will be a reduction in macronutrient vertical supply, mainly due to increased stratification, while Fe supply could potentially increase, as previously explained [111]. A shallowing trend in mixed-layer depth was observed in the southern part of the Western Antarctic Peninsula during a 24-year observation, associated with an enhanced phytoplankton carbon fixation [124], while no changes in either factor were detected in the northern part of the peninsula. A hypothetical higher irradiance would reduce Fe demand in some species [77] and possibly favor cellular Fe reallocation to Fe-bearing antioxidant enzymes. Thus, increased stratification could have a positive effect on phytoplantkon growth due to shallower mixed layers; but, increased stratification, together with acidification and deoxygenation, will also affect macronutrient availability and demand. This will alter the stoichiometry of the Fe/nutrient ratios, likely affecting existing co-limitation between Fe and macronutrients and creating new co-limitation scenarios in the future [16], with far-reaching consequences for future Fe demand, phytoplankton growth, and diversity. For example, unbalanced Fe:P ratios could substantially decrease diazotroph growth rates, and thus N fixation rates and carbon export. Future N limitation scenarios would affect differently the various phytoplankton groups, with plausible opposing trends in the Fe supply needed to support their growth (i.e., high Fe-demand diazotrophs versus a tendency for many producers towards reduced, recycled N sources) [16]. In the Fe/Si co-limited HNLC sub-Antarctic waters, a decrease in future Si supply rates is projected [100]. In low Fe waters, the restraint of vertical Si supply could shift future communities towards non-silicified phytoplankton groups, disfavoring diatoms. On the other hand, in some parts of the open SO, it is projected with medium confidence that changes in wind fields will deepen the summer mixed-layer depth [125] and raise primary productivity in the future due to increased nutrient entrainment [100,126].

Overall, there is low confidence in the predictions about the changes in future nutrient supply in the Antarctic region [111]. Furthermore, there is currently a lack of studies investigating future changes in phytoplankton cellular Fe quotas, though considerable plasticity in cellular Fe content has been observed so far, which may facilitate acclimation to future environmental changes [72,94,94,127,128]. Adaptive evolution will also play a role, helping phytoplankton to cope with a changing environment, but this subject has been rather neglected by research so far.

Leung et al. [126] predicted the trends in primary production in the SO due to climate change from 2006 to 2100 and identified a “zonally banded pattern” of phytoplankton changes in abundance and production. According to this model projection, light (influenced by summer mixed-layer depth, cloud cover, and sea-ice cover) and Fe supply were the most important factors driving phytoplankton changes in the SO, south of 40° S, while acidification was not reported as an important driver in this modelling experiment.

At present, according to the 2019 IPCC report [101], there is low confidence regarding predicted future changes in surface Fe supply (projected to increase) in the SO. This negatively affects the confidence of predicted changes in phytoplankton biomass, which is also low for the SO [111]. Low confidence in SO projections mainly arises from (1) the difficulty in mapping present Fe supply mechanisms, and (2) understanding the combined effects of multiple drivers (i.e., temperature, irradiance, nutrients, $p\mathrm{CO}_2$, pH, and grazing) on different species of phytoplankton. Currently, a common primary production trend at the circumpolar scale has not been assessed due to regional variation: if many studies point toward an increase in SO productivity, others show an opposing trend in some sectors, i.e., the subantarctic zone [100,129]. Thus, in situ long-term experiments coupled with satellite observations are clearly needed to confirm model findings regarding SO biology.

5. Discussion

Fe is an essential nutrient for all living organisms. The formulation of the landmark "Fe hypothesis" boosted research in the field, which is currently still expanding. Fe concentrations in the ocean are often very low due to biological uptake and Fe organic chemistry. This leads to the presence of HNLC regions in the world oceans, the biggest of which is in the SO. Low Fe concentrations limit primary production rates and biomass accumulation in these areas, and influence ecosystem structure and worldwide biogeochemical cycles. According to the "Fe hypothesis", atmospheric dust deposition of Fe can stimulate variations in oceanic primary productivity, thus controlling atmospheric CO_2 concentrations and hence global climate, over glacial–interglacial timescales. A contemporary application of this concept supports large-scale Fe fertilization of HNLC regions to enhance the ability of the ocean to mitigate climate change by storing anthropogenic CO_2. However, the efficacy and advisability of Fe fertilization projects is still being debated, and past in situ Fe enrichment experiments do not show a clear pattern of enhancement of the carbon export flux to the depths. What clearly emerges from the past decades of experiments, instead, is the complexity of the SO system, which we addressed in this paper with a synthetic overview of the topic.

Extensive variability exists among different regions in terms of Fe concentrations, the timing and extent of phytoplankton seasonal blooms, and susceptibility to future climate changes. Some areas, like the continental shelf region of the Ross Sea which experiences one of the largest phytoplankton blooms in the SO [38,91,92], are less Fe-stressed than other open water regions [6,38], while some other regions like East Antarctica remain relatively undersampled. The same goes for seasons: phytoplankton tends to be more Fe-stressed in summer/fall than in spring, when light is more easily limiting, and in high-Si water than in low-Si water. Considering what we have reported and summarized in this review, Fe can have a greater or lesser influence depending on environmental conditions (i.e., light, temperature, availability of other nutrients, currents, and weather) that may fluctuate considerably over small distances and timescales. Grazing is also an important regulator of primary producers biomass, but is not addressed in this review.

This environmental complexity reflects on the variability of natural populations, which is of course influenced by Fe concentrations. Even if physiological and molecular responses of various phytoplanktonic species may differ, some authors have focused on the uncovering of possible molecular indicators of Fe limitation, to understand the dynamics of Fe stress in natural populations. Chappell et al. [130], for instance, evaluated in the diatom *Thalassiosira oceanica* the expression of a gene encoding Fe-responsive flavodoxin (*FLDA1*), homolog of the Fe-regulated gene identified by Whitney et al. [131], and a gene coding an Fe-starvation-induced protein (*ISIP3*). *FLDA1* and *ISIP3* expression were inversely related to Fe concentrations and the authors suggested them as possible indicators of Fe limitation. Another work by Erdner et al. [132], focusing on seventeen species of marine phytoplankton, highlighted that ferredoxin replacement by flavodoxin was a common response to Fe stress, as was previously suggested [51]. More recently, transcriptomic studies have allowed the identification of important genes tracking the Fe status in *P. antarctica* [94] and the diatom *Pseudonitzschia* [133]. Microcosm experiments and at sea (California) also confirmed *Pseudonitzschia* biomarkers for Fe-replete and Fe-deplete conditions [133]. Similar studies may serve to identify possible biomarkers indicating severe Fe stress, not only for a specific microalgal species but also for the whole microalgal community.

As we move into a changing world, facing major ecosystem shifts, it is essential to understand how all these changes will alter the Fe cycle and predict possible cumulative enhancement, attenuation, or in some cases 'zero sum' effects. Currently, there are a variety of studies addressing this issue, but still low confidence regarding predictions of future changes in surface Fe supply and phytoplankton biomass in the SO [101,111]. Predictions in the SO are complicated by many factors, including technical sampling limitations in a harsh environment, complexity of the Fe cycle, the diversity of supply mechanisms, and the combination of multiple drivers (i.e., temperature, irradiance, nutrients, $p\mathrm{CO}_2$, pH, and grazing) on different species of phytoplankton. However, the current low-confidence projections point toward an increase in future Fe supply as a consequence of climate change, which could influence and possibly change the HNLC nature of the SO. What appears evident is that changes to a complex system, coming both from controlled large-scale experiments, or from anthropogenic climate change, will likely provoke a similarly complex, and largely unpredictable, response.

Author Contributions: Conceptualization, E.B. and M.S.; writing—original draft preparation, E.B.; writing—review and editing, E.B., C.L. and M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Italian projects: POR Campania FESR 2014–2020. Grande progetto "Risanamento Ambientale e valorizzazione dei Campi Flegrei"—Intervento del risanamento idraulico del bacino del Miseno e riapertura, sistemazione e protezione delle foci del Lago Fusaro. Monitoraggio ambientale e caratterizzazione sedimenti del Lago Fusaro e Miseno.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank the IAN/UMCES Symbol and Image Libraries (https://ian.umces.edu/media-library/symbols/; accessed on 17 December 2022) for elements in Figure 3, and the Free and Open Source Software Inkscape (http://www.inkscape.org/; last accessed on 17 December 2022) for the realization of Figures 2 and 3.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Guy, J.; Paul, G. *Écosystèmes Pélagiques Marins*; Collection d'écologie; Elsevier Masson: Paris, France; New York, NY, USA; Barcelone, Spain, 1986; ISBN 978-2-225-80760-2.
2. Knox, G.A. *Biology of the Southern Ocean*, 2nd ed.; CRC Press: Boca Raton, FL, USA, 2006; ISBN 978-0-429-11980-4.
3. Lauritano, C.; Rizzo, C.; Lo Giudice, A.; Saggiomo, M. Physiological and Molecular Responses to Main Environmental Stressors of Microalgae and Bacteria in Polar Marine Environments. *Microorganisms* **2020**, *8*, 1957. [CrossRef]
4. Martin, J.H.; Gordon, R.M.; Fitzwater, S.E. Iron in Antarctic Waters. *Nature* **1990**, *345*, 156–158. [CrossRef]
5. Morel, F.M.M.; Hudson, R.J.M.; Price, N.M. Limitation of Productivity by Trace Metals in the Sea. *Limnol. Oceanogr.* **1991**, *36*, 1742–1755. [CrossRef]
6. Fitzwater, S.E.; Johnson, K.S.; Gordon, R.M.; Coale, K.H.; Smith, W.O. Trace Metal Concentrations in the Ross Sea and Their Relationship with Nutrients and Phytoplankton Growth. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2000**, *47*, 3159–3179. [CrossRef]
7. Morel, F.M.M.; Price, N.M. The Biogeochemical Cycles of Trace Metals in the Oceans. *Science* **2003**, *300*, 944–947. [CrossRef]
8. Stoll, H. 30 Years of the Iron Hypothesis of Ice Ages. *Nature* **2020**, *578*, 370–371. [CrossRef]
9. Street, J.H.; Paytan, A. Iron, Phytoplankton Growth, and the Carbon Cycle. In *Metal Ions in Biological Systems, Volume 43—Biogeochemical Cycles of Elements*; CRC Press: Boca Raton, FL, USA, 2005; pp. 153–193. ISBN 978-0-429-16464-4.
10. Huang, Y.; Tagliabue, A.; Cassar, N. Data-Driven Modeling of Dissolved Iron in the Global Ocean. *Front. Mar. Sci.* **2022**, *9*. [CrossRef]
11. Martin, J.H. Glacial-Interglacial CO_2 Change: The Iron Hypothesis. *Paleoceanography* **1990**, *5*, 1–13. [CrossRef]
12. Loscher, B.M.; De Baar, H.J.W.; De Jong, J.T.M.; Veth, C.; Dehairs, F. The Distribution of Fe in the Antarctic Circumpolar Current. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **1997**, *44*, 143–187. [CrossRef]

13. De Baar, H.J.W.; de Jong, J.T.M.; Bakker, D.C.E.; Löscher, B.M.; Veth, C.; Bathmann, U.; Smetacek, V. Importance of Iron for Plankton Blooms and Carbon Dioxide Drawdown in the Southern Ocean. *Nature* **1995**, *373*, 412–415. [CrossRef]
14. Moore, J.K.; Abbott, M.R. Phytoplankton Chlorophyll Distributions and Primary Production in the Southern Ocean. *JGR Ocean.* **2000**, *105*, 28709–28722. [CrossRef]
15. Ryan-Keogh, T.J.; Thomalla, S.J.; Mtshali, T.N.; van Horsten, N.R.; Little, H.J. Seasonal Development of Iron Limitation in the Sub-Antarctic Zone. *Biogeosciences* **2018**, *15*, 4647–4660. [CrossRef]
16. Hutchins, D.A.; Boyd, W. Marine Phytoplankton and the Changing Ocean Iron Cycle. *Nat. Clim. Change* **2016**, *6*, 8. [CrossRef]
17. Turner, D.R.; Hunter, K.A. *The Biogeochemistry of Iron in Seawater*; Wiley: Hoboken, NJ, USA, 2001; ISBN 978-0-471-49068-5.
18. Rivaro, P.; Ardini, F.; Grotti, M.; Aulicino, G.; Cotroneo, Y.; Fusco, G.; Mangoni, O.; Bolinesi, F.; Saggiomo, M.; Celussi, M. Mesoscale Variability Related to Iron Speciation in a Coastal Ross Sea Area (Antarctica) during Summer 2014. *Chem. Ecol.* **2019**, *35*, 1–19. [CrossRef]
19. Boyd, P.W.; Arrigo, K.R.; Strzepek, R.; van Dijken, G.L. Mapping Phytoplankton Iron Utilization: Insights into Southern Ocean Supply Mechanisms. *JGR Ocean.* **2012**, *117*. [CrossRef]
20. Death, R.; Wadham, J.L.; Monteiro, F.; Le Brocq, A.M.; Tranter, M.; Ridgwell, A.; Dutkiewicz, S.; Raiswell, R. Antarctic Ice Sheet Fertilises the Southern Ocean. *Biogeosciences* **2014**, *11*, 2635–2643. [CrossRef]
21. Hawkings, J.R.; Wadham, J.L.; Tranter, M.; Raiswell, R.; Benning, L.G.; Statham, P.J.; Tedstone, A.; Nienow, P.; Lee, K.; Telling, J. Ice Sheets as a Significant Source of Highly Reactive Nanoparticulate Iron to the Oceans. *Nat. Commun.* **2014**, *5*, 3929. [CrossRef]
22. Lannuzel, D.; Vancoppenolle, M.; van der Merwe, P.; de Jong, J.; Meiners, K.M.; Grotti, M.; Nishioka, J.; Schoemann, V. Iron in Sea Ice: Review and New Insights. *Elem. Sci. Anthr.* **2016**, *4*, 000130. [CrossRef]
23. Dinniman, M.S.; St-Laurent, P.; Arrigo, K.R.; Hofmann, E.E.; Dijken, G.L. Analysis of Iron Sources in Antarctic Continental Shelf Waters. *JGR Ocean.* **2020**, *125*. [CrossRef]
24. Sedwick, P.N.; Sohst, B.M.; O'Hara, C.; Stammerjohn, S.E.; Loose, B.; Dinniman, M.S.; Buck, N.J.; Resing, J.A.; Ackley, S.F. Seasonal Dynamics of Dissolved Iron on the Antarctic Continental Shelf: Late-Fall Observations From the Terra Nova Bay and Ross Ice Shelf Polynyas. *JGR Ocean.* **2022**, *127*, e2022JC018999. [CrossRef]
25. Hoppema, M.; de Baar, H.J.W.; Fahrbach, E.; Hellmer, H.H.; Klein, B. Substantial Advective Iron Loss Diminishes Phytoplankton Production in the Antarctic Zone. *Glob. Biogeochem. Cycles* **2003**, *17*. [CrossRef]
26. Watson, A.J.; Bakker, D.C.; Ridgwell, A.J.; Boyd, P.W.; Law, C.S. Effect of Iron Supply on Southern Ocean CO_2 Uptake and Implications for Glacial Atmospheric CO_2. *Nature* **2000**, *407*, 730–733. [CrossRef] [PubMed]
27. Hiscock, M.R.; Marra, J.; Smith, W.O.; Goericke, R.; Measures, C.; Vink, S.; Olson, R.J.; Sosik, H.M.; Barber, R.T. Primary Productivity and Its Regulation in the Pacific Sector of the Southern Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2003**, *50*, 533–558. [CrossRef]
28. Smith, A.J.R.; Ratnarajah, L.; Holmes, T.M.; Wuttig, K.; Townsend, A.T.; Westwood, K.; Cox, M.; Bell, E.; Nicol, S.; Lannuzel, D. Circumpolar Deep Water and Shelf Sediments Support Late Summer Microbial Iron Remineralization. *Glob. Biogeochem. Cycles* **2021**, *35*, e2020GB006921. [CrossRef]
29. Sedwick, P.N.; Bowie, A.R.; Trull, T.W. Dissolved Iron in the Australian Sector of the Southern Ocean (CLIVAR SR3 Section): Meridional and Seasonal Trends. *Deep. Sea Res. Part I Oceanogr. Res. Pap.* **2008**, *55*, 911–925. [CrossRef]
30. Gerringa, L.J.A.; Alderkamp, A.-C.; Laan, P.; Thuróczy, C.-E.; De Baar, H.J.W.; Mills, M.M.; van Dijken, G.L.; van Haren, H.; Arrigo, K.R. Iron from Melting Glaciers Fuels the Phytoplankton Blooms in Amundsen Sea (Southern Ocean): Iron Biogeochemistry. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2012**, *71–76*, 16–31. [CrossRef]
31. Cullen, J.J. Hypotheses to Explain High-Nutrient Conditions in the Open Sea. *Limnol. Oceanogr.* **1991**, *36*, 1578–1599. [CrossRef]
32. Minas, H.; Minas, M. Net Community Production in High Nutrient-Low Chlorophyll Waters of the Tropical and Antarctic Oceans - Grazing vs Iron Hypothesis. *Oceanol. Acta* **1992**, *15*, 145–162.
33. De Baar, H.J.W.; Buma, A.J.G.; Nolting, R.F.; Cadee, G.C.; Jacques, G.; Treguer, P.J. On Iron Limitation of the Southern Ocean: Experimental Observations in the Weddell and Scotia Seas. *Mar. Ecol. Prog. Ser.* **1990**, *65*, 105–122. [CrossRef]
34. 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.; et al. Testing the Iron Hypothesis in Ecosystems of the Equatorial Pacific Ocean. *Nature* **1994**, *371*, 123–129. [CrossRef]
35. 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.; et al. A Massive Phytoplankton Bloom Induced by an Ecosystem-Scale Iron Fertilization Experiment in the Equatorial Pacific Ocean. *Nature* **1996**, *383*, 495–501. [CrossRef]
36. De Baar, H.J.W.; de Jong, J.T.M.; Nolting, R.F.; Timmermans, K.R.; van Leeuwe, M.A.; Bathmann, U.; Rutgers van der Loeff, M.; Sildam, J. Low Dissolved Fe and the Absence of Diatom Blooms in Remote Pacific Waters of the Southern Ocean. *Mar. Chem.* **1999**, *66*, 1–34. [CrossRef]
37. Moore, C.M.; Seeyave, S.; Hickman, A.E.; Allen, J.T.; Lucas, M.I.; Planquette, H.; Pollard, R.T.; Poulton, A.J. Iron–Light Interactions during the CROZet Natural Iron Bloom and EXport Experiment (CROZEX) I: Phytoplankton Growth and Photophysiology. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2007**, *54*, 2045–2065. [CrossRef]
38. Coale, K.H.; Wang, X.; Tanner, S.J.; Johnson, K.S. Phytoplankton Growth and Biological Response to Iron and Zinc Addition in the Ross Sea and Antarctic Circumpolar Current along 170° W. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2003**, *50*, 635–653. [CrossRef]

39. Timmermans, K.; van Leeuwe, M.; de Jong, J.; McKay, R.; Nolting, R.; Witte, H.; van Ooyen, J.; Swagerman, M.; Kloosterhuis, H.; de Baar, H. Iron Stress in the Pacific Region of the Southern Ocean:Evidence from Enrichment Bioassays. *Mar. Ecol. Prog. Ser.* **1998**, *166*, 27–41. [CrossRef]
40. Öztürk, M.; Croot, P.L.; Bertilsson, S.; Abrahamsson, K.; Karlson, B.; David, R.; Fransson, A.; Sakshaug, E. Iron Enrichment and Photoreduction of Iron under UV and PAR in the Presence of Hydroxycarboxylic Acid: Implications for Phytoplankton Growth in the Southern Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2004**, *51*, 2841–2856. [CrossRef]
41. 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.; et al. Mesoscale Iron Enrichment Experiments 1993-2005: Synthesis and Future Directions. *Science* **2007**, *315*, 612–617. [CrossRef]
42. De Baar, H.J.W.; Boyd, P.; Coale, K.; Landry, M.; Tsuda, A.; Assmy, P.; Bakker, D.; Bozec, Y.; Barber, R.; Brzezinski, M.; et al. Synthesis of Iron Fertilization Experiments: From the Iron Age in the Age of Enlightenment. *JGR Atmos.* **2005**. [CrossRef]
43. Yoon, J.-E.; Yoo, K.-C.; Macdonald, A.M.; Yoon, H.-I.; Park, K.-T.; Yang, E.J.; Kim, H.-C.; Lee, J.I.; Lee, M.K.; Jung, J.; et al. Ocean Iron Fertilization Experiments – Past, Present, and Future Looking to a Future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) Project. *Biogeosciences* **2018**, *15*, 5847–5889. [CrossRef]
44. Blain, S.; Tréguer, P.; Belviso, S.; Bucciarelli, E.; Denis, M.; Desabre, S.; Fiala, M.; Martin-Jezequel, V.; Fèvre, J.; Mayzaud, P.; et al. Biogeochemical Study of an Island Mass Effect in the Context of the Iron Hypothesis in the Southern Ocean. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2001**, *48*, 163–187. [CrossRef]
45. Blain, S.; Quéguiner, B.; Armand, L.; Belviso, S.; Bombled, B.; Bopp, L.; Bowie, A.; Brunet, C.; Brussaard, C.; Carlotti, F.; et al. Effect of Natural Iron Fertilization on Carbon Sequestration in the Southern Ocean. *Nature* **2007**, *446*, 1070–1074. [CrossRef] [PubMed]
46. Blain, S.; Sarthou, G.; Laan, P. Distribution of Dissolved Iron during the Natural Iron-Fertilization Experiment KEOPS (Kerguelen Plateau, Southern Ocean). *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2008**, *55*, 594–605. [CrossRef]
47. Moore, C.M.; Hickman, A.E.; Poulton, A.J.; Seeyave, S.; Lucas, M.I. Iron-Light Interactions during the CROZet Natural Iron Bloom and EXport Experiment (CROZEX): II-Taxonomic Responses and Elemental Stoichiometry. *Deep-Sea Res. Part II Top. Stud. Oceanogr.* **2007**, *54*, 2066–2084. [CrossRef]
48. Cassar, N.; Bender, M.L.; Barnett, B.A.; Fan, S.; Moxim, W.J.; Levy, H.; Tilbrook, B. The Southern Ocean Biological Response to Aeolian Iron Deposition. *Science* **2007**, *317*, 1067–1070. [CrossRef]
49. Mills, M.M.; Alderkamp, A.-C.; Thuróczy, C.-E.; van Dijken, G.L.; Laan, P.; de Baar, H.J.W.; Arrigo, K.R. Phytoplankton Biomass and Pigment Responses to Fe Amendments in the Pine Island and Amundsen Polynyas. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2012**, *71–76*, 61–76. [CrossRef]
50. Arrigo, K.R.; DiTullio, G.R.; Dunbar, R.B.; Robinson, D.H.; VanWoert, M.; Worthen, D.L.; Lizotte, M.P. Phytoplankton Taxonomic Variability in Nutrient Utilization and Primary Production in the Ross Sea. *J. Geophys. Res. Ocean.* **2000**, *105*, 8827–8846. [CrossRef]
51. Maucher, J.M.; DiTullio, G.R. Flavodoxin as a Diagnostic Indicator of Chronic Iron Limitation in the Ross Sea and New Zealand Sector of the Southern Ocean. *Antarct. Res. Ser.* **2003**, *78*, 11.
52. 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.; et al. A Mesoscale Phytoplankton Bloom in the Polar Southern Ocean Stimulated by Iron Fertilization. *Nature* **2000**, *407*, 695–702. [CrossRef]
53. Boyd, P.W.; Law, C.S. The Southern Ocean Iron RElease Experiment (SOIREE)—Introduction and Summary. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2001**, *48*, 2425–2438. [CrossRef]
54. Maldonado, M.T.; Boyd, P.W.; LaRoche, J.; Strzepek, R.; Waite, A.; Bowie, A.R.; Croot, P.L.; Frew, R.D.; Price, N.M. Iron Uptake and Physiological Response of Phytoplankton during a Mesoscale Southern Ocean Iron Enrichment. *Limnol. Oceanogr.* **2001**, *46*, 1802–1808. [CrossRef]
55. Gervais, F.; Riebesell, U.; Gorbunov, M.Y. Changes in Primary Productivity and Chlorophyll a in Response to Iron Fertilization in the Southern Polar Frontal Zone. *Limnol. Oceanogr.* **2002**, *47*, 1324–1335. [CrossRef]
56. 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.; et al. Southern Ocean Iron Enrichment Experiment: Carbon Cycling in High- and Low-Si Waters. *Science* **2004**, *304*, 408–414. [CrossRef] [PubMed]
57. Buesseler, K.O.; Andrews, J.E.; Pike, S.M.; Charette, M.A. The Effects of Iron Fertilization on Carbon Sequestration in the Southern Ocean. *Science* **2004**, *304*, 414–417. [CrossRef]
58. Hoffmann, L.J.; Peeken, I.; Lochte, K.; Assmy, P.; Veldhuis, M. Different Reactions of Southern Ocean Phytoplankton Size Classes to Iron Fertilization. *Limnol. Oceanogr.* **2006**, *51*, 1217–1229. [CrossRef]
59. 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.; et al. The SOLAS Air–Sea Gas Exchange Experiment (SAGE) 2004. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2011**, *58*, 753–763. [CrossRef]
60. 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.; et al. Iron Fertilization Enhanced Net Community Production but Not Downward Particle Flux during the Southern Ocean Iron Fertilization Experiment LOHAFEX. *Glob. Biogeochem. Cycles* **2013**, *27*, 871–881. [CrossRef]
61. Smetacek, V.; 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); Alfred Wegener Institute for Polar and Marine Research: Bremerhaven, Germany, 2010; Volume 613.

62. 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.; et al. Southern Ocean Deep-Water Carbon Export Enhanced by Natural Iron Fertilization. *Nature* **2009**, *457*, 577–580. [CrossRef]
63. Christaki, U.; Lefèvre, D.; Georges, C.; Colombet, J.; Catala, P.; Courties, C.; Sime-Ngando, T.; Blain, S.; Obernosterer, I. Microbial Food Web Dynamics during Spring Phytoplankton Blooms in the Naturally Iron-Fertilized Kerguelen Area (Southern Ocean). *Biogeosciences* **2014**, *11*, 6739–6753. [CrossRef]
64. Boyd, P.; LaRoche, J.; Gall, M.; Frew, R.; McKay, R.M.L. Role of Iron, Light, and Silicate in Controlling Algal Biomass in Subantarctic Waters SE of New Zealand. *JGR Ocean.* **1999**, *104*, 13395–13408. [CrossRef]
65. Franck, V.M.; Brzezinski, M.A.; Coale, K.H.; Nelson, D.M. Iron and Silicic Acid Concentrations Regulate Si Uptake North and South of the Polar Frontal Zone in the Pacific Sector of the Southern Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2000**, *47*, 3315–3338. [CrossRef]
66. Boyd, P.W.; Crossley, A.C.; DiTullio, G.R.; Griffiths, F.B.; Hutchins, D.A.; Queguiner, B.; Sedwick, P.N.; Trull, T.W. Control of Phytoplankton Growth by Iron Supply and Irradiance in the Subantarctic Southern Ocean: Experimental Results from the SAZ Project. *JGR Ocean.* **2001**, *106*, 31573–31583. [CrossRef]
67. Hutchins, D.A.; Sedwick, P.N.; DiTullio, G.R.; Boyd, P.W.; Quéguiner, B.; Griffiths, F.B.; Crossley, C. Control of Phytoplankton Growth by Iron and Silicic Acid Availability in the Subantarctic Southern Ocean: Experimental Results from the SAZ Project. *J. Geophys. Res. Ocean.* **2001**, *106*, 31559–31572. [CrossRef]
68. Hinz, D.J.; Nielsdóttir, M.C.; Korb, R.E.; Whitehouse, M.J.; Poulton, A.J.; Moore, C.M.; Achterberg, E.P.; Bibby, T.S. Responses of Microplankton Community Structure to Iron Addition in the Scotia Sea. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2012**, *59–60*, 36–46. [CrossRef]
69. Alderkamp, A.-C.; van Dijken, G.L.; Lowry, K.E.; Connelly, T.L.; Lagerström, M.; Sherrell, R.M.; Haskins, C.; Rogalsky, E.; Schofield, O.; Stammerjohn, S.E.; et al. Fe Availability Drives Phytoplankton Photosynthesis Rates during Spring Bloom in the Amundsen Sea Polynya, Antarctica. *Elem. Sci. Anthr.* **2015**, *3*, 000043. [CrossRef]
70. Ryan-Keogh, T.J.; DeLizo, L.M.; Smith, W.O.; Sedwick, P.N.; McGillicuddy, D.J.; Moore, C.M.; Bibby, T.S. Temporal Progression of Photosynthetic-Strategy in Phytoplankton in the Ross Sea, Antarctica. *J. Mar. Syst.* **2017**, *166*, 87–96. [CrossRef]
71. Viljoen, J.J.; Philibert, R.; Van Horsten, N.; Mtshali, T.; Roychoudhury, A.N.; Thomalla, S.; Fietz, S. Phytoplankton Response in Growth, Photophysiology and Community Structure to Iron and Light in the Polar Frontal Zone and Antarctic Waters. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2018**, *141*, 118–129. [CrossRef]
72. Alderkamp, A.-C.; van Dijken, G.L.; Lowry, K.E.; Lewis, K.M.; Joy-Warren, H.L.; van de Poll, W.; Laan, P.; Gerringa, L.; Delmont, T.O.; Jenkins, B.D.; et al. Effects of Iron and Light Availability on Phytoplankton Photosynthetic Properties in the Ross Sea. *Mar. Ecol. Prog. Ser.* **2019**, *621*, 33–50. [CrossRef]
73. Vives, C.R.; Schallenberg, C.; Strutton, P.G.; Westwood, K.J. Iron and Light Limitation of Phytoplankton Growth off East Antarctica. *J. Mar. Syst.* **2022**, *234*, 103774. [CrossRef]
74. Moore, J.K.; Doney, S.C.; Glover, D.M.; Fung, I.Y. Iron Cycling and Nutrient-Limitation Patterns in Surface Waters of the World Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2001**, *49*, 463–507. [CrossRef]
75. Boyd, P.W.; Strzepek, R.; Fu, F.; Hutchins, D.A. Environmental Control of Open-Ocean Phytoplankton Groups: Now and in the Future. *Limnol. Oceanogr.* **2010**, *55*, 1353–1376. [CrossRef]
76. Sunda, W.G.; Huntsman, S.A. Interrelated Influence of Iron, Light and Cell Size on Marine Phytoplankton Growth. *Nature* **1997**, *390*, 389–392. [CrossRef]
77. Strzepek, R.F.; Hunter, K.A.; Frew, R.D.; Harrison, P.J.; Boyd, P.W. Iron-Light Interactions Differ in Southern Ocean Phytoplankton. *Limnol. Oceanogr.* **2012**, *57*, 1182–1200. [CrossRef]
78. Moreno, C.M.; Lin, Y.; Davies, S.; Monbureau, E.; Cassar, N.; Marchetti, A. Examination of Gene Repertoires and Physiological Responses to Iron and Light Limitation in Southern Ocean Diatoms. *Polar Biol.* **2018**, *41*, 679–696. [CrossRef]
79. Strzepek, R.F.; Boyd, P.W.; Sunda, W.G. Photosynthetic Adaptation to Low Iron, Light, and Temperature in Southern Ocean Phytoplankton. *Proc. Natl. Acad. Sci. USA* **2019**, *116*, 4388–4393. [CrossRef] [PubMed]
80. Coale, T.H.; Bertrand, E.M.; Lampe, R.H.; Allen, A.E. Molecular Mechanisms Underlying Micronutrient Utilization in Marine Diatoms. In *The Molecular Life of Diatoms*; Falciatore, A., Mock, T., Eds.; Springer International Publishing: Cham, Switzerland, 2022; pp. 567–604. ISBN 978-3-030-92499-7.
81. Rose, J.M.; Feng, Y.; DiTullio, G.R.; Dunbar, R.B.; Hare, C.E.; Lee, P.A.; Lohan, M.; Long, M.; Smith, W.O., Jr.; Sohst, B.; et al. Synergistic Effects of Iron and Temperature on Antarctic Phytoplankton and Microzooplankton Assemblages. *Biogeosciences* **2009**, *6*, 3131–3147. [CrossRef]
82. Zhu, Z.; Xu, K.; Fu, F.; Spackeen, J.; Bronk, D.; Hutchins, D. A Comparative Study of Iron and Temperature Interactive Effects on Diatoms and *Phaeocystis Antarctica* from the Ross Sea, Antarctica. *Mar. Ecol. Prog. Ser.* **2016**, *550*, 39–51. [CrossRef]
83. Jabre, L.J.; Allen, A.E.; McCain, J.S.P.; McCrow, J.P.; Tenenbaum, N.; Spackeen, J.L.; Sipler, R.E.; Green, B.R.; Bronk, D.A.; Hutchins, D.A.; et al. Molecular Underpinnings and Biogeochemical Consequences of Enhanced Diatom Growth in a Warming Southern Ocean. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2107238118. [CrossRef]
84. Booth, B.C.; Lewin, J.; Postel, J.R. Temporal Variation in the Structure of Autotrophic and Heterotrophic Communities in the Subarctic Pacific. *Prog. Oceanogr.* **1993**, *32*, 57–99. [CrossRef]

85. Mangoni, O.; Saggiomo, V.; Bolinesi, F.; Margiotta, F.; Budillon, G.; Cotroneo, Y.; Misic, C.; Rivaro, P.; Saggiomo, M. Phytoplankton Blooms during Austral Summer in the Ross Sea, Antarctica: Driving Factors and Trophic Implications. *PLoS ONE* **2017**, *12*, e0176033. [CrossRef]
86. Kohut, J.T.; Kustka, A.B.; Hiscock, M.R.; Lam, P.J.; Measures, C.; Milligan, A.; White, A.; Carvalho, F.; Hatta, M.; Jones, B.M.; et al. Mesoscale Variability of the Summer Bloom over the Northern Ross Sea Shelf: A Tale of Two Banks. *J. Mar. Syst.* **2017**, *166*, 50–60. [CrossRef]
87. Saggiomo, V.; Catalano, G.; Mangoni, O.; Budillon, G.; Carrada, G.C. Primary Production Processes in Ice-Free Waters of the Ross Sea (Antarctica) during the Austral Summer 1996. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2002**, *49*, 1787–1801. [CrossRef]
88. Hatta, M.; Measures, C.I.; Lam, P.J.; Ohnemus, D.C.; Auro, M.E.; Grand, M.M.; Selph, K.E. The Relative Roles of Modified Circumpolar Deep Water and Benthic Sources in Supplying Iron to the Recurrent Phytoplankton Blooms above Pennell and Mawson Banks, Ross Sea, Antarctica. *J. Mar. Syst.* **2017**, *166*, 61–72. [CrossRef]
89. Jacobs, S.S.; Giulivi, C.F. Large Multidecadal Salinity Trends near the Pacific–Antarctic Continental Margin. *J. Clim.* **2010**, *23*, 4508–4524. [CrossRef]
90. Budillon, G.; Castagno, P.; Aliani, S.; Spezie, G.; Padman, L. Thermohaline Variability and Antarctic Bottom Water Formation at the Ross Sea Shelf Break. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2011**, *58*, 1002–1018. [CrossRef]
91. Bolinesi, F.; Saggiomo, M.; Ardini, F.; Castagno, P.; Cordone, A.; Fusco, G.; Rivaro, P.; Saggiomo, V.; Mangoni, O. Spatial-Related Community Structure and Dynamics in Phytoplankton of the Ross Sea, Antarctica. *Front. Mar. Sci.* **2020**, *7*. [CrossRef]
92. Saggiomo, M.; Escalera, L.; Saggiomo, V.; Bolinesi, F.; Mangoni, O. Phytoplankton Blooms Below the Antarctic Landfast Ice During the Melt Season Between Late Spring and Early Summer. *J. Phycol.* **2021**, *57*, 541–550. [CrossRef] [PubMed]
93. Rivaro, P.; Ianni, C.; Langone, L.; Ori, C.; Aulicino, G.; Cotroneo, Y.; Saggiomo, M.; Mangoni, O. Physical and Biological Forcing of Mesoscale Variability in the Carbonate System of the Ross Sea (Antarctica) during Summer 2014. *J. Mar. Syst.* **2017**, *166*, 144–158. [CrossRef]
94. Bender, S.J.; Moran, D.M.; McIlvin, M.R.; Zheng, H.; McCrow, J.P.; Badger, J.; DiTullio, G.R.; Allen, A.E.; Saito, M.A. Colony Formation in Phaeocystis Antarctica: Connecting Molecular Mechanisms with Iron Biogeochemistry. *Biogeosciences* **2018**, *15*, 4923–4942. [CrossRef]
95. Martínez-García, A.; Sigman, D.M.; Ren, H.; Anderson, R.F.; Straub, M.; Hodell, D.A.; Jaccard, S.L.; Eglinton, T.I.; Haug, G.H. Iron Fertilization of the Subantarctic Ocean During the Last Ice Age. *Science* **2014**, *343*, 1347–1350. [CrossRef]
96. Smetacek, V.; Naqvi, S.W.A. The next Generation of Iron Fertilization Experiments in the Southern Ocean. *Phil. Trans. R. Soc. A.* **2008**, *366*, 3947–3967. [CrossRef]
97. Denman, K.L. Climate Change, Ocean Processes and Ocean Iron Fertilization. *Mar. Ecol. Prog. Ser.* **2008**, *364*, 219–225. [CrossRef]
98. Smetacek, V.; Klaas, C.; Strass, V.H.; Assmy, P.; Montresor, M.; Cisewski, B.; Savoye, N.; Webb, A.; d'Ovidio, F.; Arrieta, J.M.; et al. Deep Carbon Export from a Southern Ocean Iron-Fertilized Diatom Bloom. *Nature* **2012**, *487*, 313–319. [CrossRef]
99. Tripathy, S.C.; Jena, B. Iron-Stimulated Phytoplankton Blooms in the Southern Ocean: A Brief Review. *Remote Sens. Earth Syst. Sci.* **2019**, *2*, 64–77. [CrossRef]
100. IPCC. Climate Change 2022: Impacts, Adaptation and Vulnerability. In *Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2022; p. 3056.
101. Bindoff, N.L.; Cheung, W.W.L.; Kairo, J.G.; Arístegui, J.; Guinder, V.A.; Hallberg, R.; Hilmi, N.; Jiao, N.; Karim, M.S.; Levin, L.; et al. Changing Ocean, Marine Ecosystems, and Dependent Communities. In *IPCC Special Report on the Ocean and Cryosphere in a Changing Climate*; Pörtner, H.-O., Roberts, D.C., Masson-Delmotte, V., Zhai, P., Tignor, M., Poloczanska, E., Mintenbeck, K., Alegría, A., Nicolai, M., Okem, A., et al., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2019.
102. IPCC. Climate Change 2007: Mitigation. In *Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2007.
103. Lambert, F.; Tagliabue, A.; Shaffer, G.; Lamy, F.; Winckler, G.; Farias, L.; Gallardo, L.; De Pol-Holz, R. Dust Fluxes and Iron Fertilization in Holocene and Last Glacial Maximum Climates. *Geophys. Res. Lett.* **2015**, *42*, 6014–6023. [CrossRef]
104. Boyd, P.W.; Claustre, H.; Levy, M.; Siegel, D.A.; Weber, T. Multi-Faceted Particle Pumps Drive Carbon Sequestration in the Ocean. *Nature* **2019**, *568*, 327–335. [CrossRef] [PubMed]
105. Tagliabue, A.; Bowie, A.R.; Boyd, P.W.; Buck, K.N.; Johnson, K.S.; Saito, M.A. The Integral Role of Iron in Ocean Biogeochemistry. *Nature* **2017**, *543*, 51–59. [CrossRef]
106. Oschlies, A.; Koeve, W.; Rickels, W.; Rehdanz, K. Side Effects and Accounting Aspects of Hypothetical Large-Scale Southern Ocean Iron Fertilization. *Biogeosciences* **2010**, *7*, 4017–4035. [CrossRef]
107. Fuhrman, J.A.; Capone, D.G. Possible Biogeochemical Consequences of Ocean Fertilization. *Limnol. Oceanogr.* **1991**, *36*, 1951–1959. [CrossRef]
108. Silver, M.W.; Bargu, S.; Coale, S.L.; Benitez-Nelson, C.R.; Garcia, A.C.; Roberts, K.J.; Sekula-Wood, E.; Bruland, K.W.; Coale, K.H. Toxic Diatoms and Domoic Acid in Natural and Iron Enriched Waters of the Oceanic Pacific. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 20762–20767. [CrossRef]
109. Trick, C.G.; Bill, B.D.; Cochlan, W.P.; Wells, M.L.; Trainer, V.L.; Pickell, L.D. Iron Enrichment Stimulates Toxic Diatom Production in High-Nitrate, Low-Chlorophyll Areas. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 5887–5892. [CrossRef]

110. Constable, A.J.; Melbourne-Thomas, J.; Corney, S.P.; Arrigo, K.R.; Barbraud, C.; Barnes, D.K.A.; Bindoff, N.L.; Boyd, P.W.; Brandt, A.; Costa, D.P.; et al. Climate Change and Southern Ocean Ecosystems I: How Changes in Physical Habitats Directly Affect Marine Biota. *Glob. Change Biol.* **2014**, *20*, 3004–3025. [CrossRef]
111. Meredith, M.; Sommerkorn, M.; Cassotta, S.; Derksen, C.; Ekaykin, A.; Hollowed, A.; Kofinas, G.; Mackintosh, A.; Melbourne-Thomas, J.; Muelbert, M.M.C.; et al. Polar Regions. In *IPCC Special Report on the Ocean and Cryosphere in a Changing Climate Climate*; Pörtner, H.-O., Roberts, D.C., Masson-Delmotte, V., Zhai, P., Tignor, M., Poloczanska, E., Mintenbeck, K., Alegría, A., Nicolai, M., Okem, A., et al., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2019.
112. Shadwick, E.H.; Rintoul, S.R.; Tilbrook, B.; Williams, G.D.; Young, N.; Fraser, A.D.; Marchant, H.; Smith, J.; Tamura, T. Glacier Tongue Calving Reduced Dense Water Formation and Enhanced Carbon Uptake. *Geophys. Res. Lett.* **2013**, *40*, 904–909. [CrossRef]
113. Cape, M.R.; Vernet, M.; Kahru, M.; Spreen, G. Polynya Dynamics Drive Primary Production in the Larsen A and B Embayments Following Ice Shelf Collapse. *J. Geophys. Res. Ocean.* **2014**, *119*, 572–594. [CrossRef]
114. Monien, P.; Lettmann, K.A.; Monien, D.; Asendorf, S.; Wölfl, A.-C.; Lim, C.H.; Thal, J.; Schnetger, B.; Brumsack, H.-J. Redox Conditions and Trace Metal Cycling in Coastal Sediments from the Maritime Antarctic. *Geochim. Cosmochim. Acta* **2014**, *141*, 26–44. [CrossRef]
115. Duprat, L.P.A.M.; Bigg, G.R.; Wilton, D.J. Enhanced Southern Ocean Marine Productivity Due to Fertilization by Giant Icebergs. *Nat. Geosci.* **2016**, *9*, 219–221. [CrossRef]
116. Arrigo, K.R.; van Dijken, G.L. Continued Increases in Arctic Ocean Primary Production. *Prog. Oceanogr.* **2015**, *136*, 60–70. [CrossRef]
117. Duprat, L.; Kanna, N.; Janssens, J.; Roukaerts, A.; Deman, F.; Townsend, A.T.; Meiners, K.M.; van der Merwe, P.; Lannuzel, D. Enhanced Iron Flux to Antarctic Sea Ice via Dust Deposition From Ice-Free Coastal Areas. *J. Geophys. Res. Ocean.* **2019**, *124*, 8538–8557. [CrossRef]
118. Van der Merwe, P.; Wuttig, K.; Holmes, T.; Trull, T.W.; Chase, Z.; Townsend, A.T.; Goemann, K.; Bowie, A.R. High Lability Fe Particles Sourced From Glacial Erosion Can Meet Previously Unaccounted Biological Demand: Heard Island, Southern Ocean. *Front. Mar. Sci.* **2019**, *6*, 332. [CrossRef]
119. Xu, K.; Fu, F.-X.; Hutchins, D.A. Comparative Responses of Two Dominant Antarctic Phytoplankton Taxa to Interactions between Ocean Acidification, Warming, Irradiance, and Iron Availability. *Limnol. Oceanogr.* **2014**, *59*, 1919–1931. [CrossRef]
120. Boyd, P.W.; Dillingham, P.W.; McGraw, C.M.; Armstrong, E.A.; Cornwall, C.E.; Feng, Y.-Y.; Hurd, C.L.; Gault-Ringold, M.; Roleda, M.Y.; Timmins-Schiffman, E.; et al. Physiological Responses of a Southern Ocean Diatom to Complex Future Ocean Conditions. *Nat. Clim. Change* **2016**, *6*, 207–213. [CrossRef]
121. Feng, Y.; Hare, C.E.; Rose, J.M.; Handy, S.M.; DiTullio, G.R.; Lee, P.A.; Smith, W.O.; Peloquin, J.; Tozzi, S.; Sun, J.; et al. Interactive Effects of Iron, Irradiance and CO2 on Ross Sea Phytoplankton. *Deep Sea Res. Part I Oceanogr. Res. Pap.* **2010**, *57*, 368–383. [CrossRef]
122. Hoppe, C.J.M.; Hassler, C.S.; Payne, C.D.; Tortell, P.D.; Rost, B.; Trimborn, S. Iron Limitation Modulates Ocean Acidification Effects on Southern Ocean Phytoplankton Communities. *PLoS ONE* **2013**, *8*, e79890. [CrossRef]
123. Deppeler, S.; Petrou, K.; Schulz, K.G.; Westwood, K.; Pearce, I.; McKinlay, J.; Davidson, A. Ocean Acidification of a Coastal Antarctic Marine Microbial Community Reveals a Critical Threshold for CO_2 Tolerance in Phytoplankton Productivity. *Biogeosciences* **2018**, *15*, 209–231. [CrossRef]
124. Schofield, O.; Brown, M.; Kohut, J.; Nardelli, S.; Saba, G.; Waite, N.; Ducklow, H. Changes in the Upper Ocean Mixed Layer and Phytoplankton Productivity along the West Antarctic Peninsula. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2018**, *376*, 20170173. [CrossRef]
125. Panassa, E.; Völker, C.; Wolf-Gladrow, D.; Hauck, J. Drivers of Interannual Variability of Summer Mixed Layer Depth in the Southern Ocean Between 2002 and 2011. *J. Geophys. Res. Ocean.* **2018**, *123*, 5077–5090. [CrossRef]
126. Leung, S.; Cabré, A.; Marinov, I. A Latitudinally Banded Phytoplankton Response to 21st Century Climate Change in the Southern Ocean across the CMIP5 Model Suite. *Biogeosciences* **2015**, *12*, 5715–5734. [CrossRef]
127. King, A.L.; Sañudo-Wilhelmy, S.A.; Boyd, P.W.; Twining, B.S.; Wilhelm, S.W.; Breene, C.; Ellwood, M.J.; Hutchins, D.A. A Comparison of Biogenic Iron Quotas during a Diatom Spring Bloom Using Multiple Approaches. *Biogeosciences* **2012**, *9*, 667–687. [CrossRef]
128. Luxem, K.E.; Ellwood, M.J.; Strzepek, R.F. Intraspecific Variability in *Phaeocystis Antarctica*'s Response to Iron and Light Stress. *PLoS ONE* **2017**, *12*, e0179751. [CrossRef]
129. Pinkerton, M.H.; Boyd, P.W.; Deppeler, S.; Hayward, A.; Höfer, J.; Moreau, S. Evidence for the Impact of Climate Change on Primary Producers in the Southern Ocean. *Front. Ecol. Evol.* **2021**, *9*. [CrossRef]
130. Chappell, P.D.; Whitney, L.P.; Wallace, J.R.; Darer, A.I.; Jean-Charles, S.; Jenkins, B.D. Genetic Indicators of Iron Limitation in Wild Populations of *Thalassiosira Oceanica* from the Northeast Pacific Ocean. *ISME J.* **2015**, *9*, 592–602. [CrossRef]
131. Whitney, L.; Lins, J.; Hughes, M.; Wells, M.; Chappell, P.; Jenkins, B. Characterization of Putative Iron Responsive Genes as Species-Specific Indicators of Iron Stress in Thalassiosiroid Diatoms. *Front. Microbiol.* **2011**, *2*. [CrossRef] [PubMed]

132. Erdner, D.L.; Price, N.M.; Doucette, G.J.; Peleato, M.L.; Anderson, D.M. Characterization of Ferredoxin and Flavodoxin as Markers of Iron Limitation in Marine Phytoplankton. *Mar. Ecol. Prog. Ser.* **1999**, *184*, 43–53. [CrossRef]
133. Marchetti, A.; Moreno, C.M.; Cohen, N.R.; Oleinikov, I.; de Long, K.; Twining, B.S.; Armbrust, E.V.; Lampe, R.H. Development of a Molecular-Based Index for Assessing Iron Status in Bloom-Forming Pennate Diatoms. *J. Phycol.* **2017**, *53*, 820–832. [CrossRef] [PubMed]