REGULAR ISSUE FEATURE

A New Database to Explore the Findings from Large-Scale Ocean Iron Enrichment Experiments

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ABSTRACT. Some of the largest scientific manipulation experiments conducted on our planet have enriched broad swaths of the surface ocean with iron. Surface ocean signatures of these iron enrichment experiments have covered areas up to > 1,000 km^2 and have been conspicuous from space. Twelve of these multidisciplinary studies have been conducted since the early 1990s in three specific ocean regions—the Southern Ocean, and equatorial and sub-Arctic areas of the Pacific Ocean—where plant nutrients are perennially high (termed high nutrient low chlorophyll, or HNLC). In addition, a combined phosphorus and iron enrichment experiment was conducted in the oligotrophic North Atlantic Ocean. Together, these studies represent a unique set of physical, chemical, optical, biological, and ecological data. The richness of these data sets is captured in an open-access relational database at the Biological and Chemical Oceanography Data Management Office (BCO_DMO; http://osprey.bco-dmo.org/program.cfm?flag=viewp&id=10&sortby=program). It is a product of Working Group 131 (The Legacy of in situ Iron Enrichment: Data Compilation and Modeling; http://www.scor-int.org/Working_Groups/wg131.htm) of the Scientific Committee on Oceanic Research. The purpose of this article is to make the wider community aware of this resource. It also presents the merits and provides examples of the utility of this database for exploring emerging topics in oceanography, such as the links between ecosystem processes and biogeochemical cycles; the feasibility and many side effects of oceanic geoengineering; and how understanding the coupling among physical, chemical, and biological processes at the mesoscale can inform the emerging field of submesoscale biogeochemistry.

INTRODUCTION

For the last 80 years, oceanographers have been puzzled about why certain oceanic regions are characterized by low stocks of phytoplankton despite a perennial excess of nutrients such as nitrate (De Baar, 1994). For example, Hart (1934) observed this paradox in the Southern Ocean, and it is now commonly referred to as the HNLC (high nutrient low chlorophyll) condition (Chisholm and Morel, 1991). There has been considerable progress since the late 1980s in revisiting the Southern Ocean paradox. Martin and Fitzwater (1988) revealed that adding iron to the resident phytoplankton in the HNLC waters of the sub-Arctic Northeast Pacific resulted in a striking increase in phytoplankton stocks to levels equivalent to a bloom, and a concomitant decrease in nutrient concentrations. However, others, such as Banse (1991), offered a "nonferrous" alternative explanation for such trends, questioning whether, given the small-volume (i.e., less than 25 L) incubation vessels used in these experiments, artifactual exclusion of zooplankton grazers, rather than iron enrichment, was shifting the balance toward boosting phytoplankton growth and hence stocks.

John Martin used shipboard experimental findings, including those described in Martin and Fitzwater (1988), to develop the Iron Hypothesis (Martin, 1990), which drew widespread attention to the potential links between changes in iron supply to the ocean in the geological past and consequent modulation of biological productivity. Changes to marine productivity led to alteration of the ocean's carbon cycle, which contributed as much as 30% to roughly 80 µatm shifts (i.e., from 280 to 200 µatm toward the interglacials) in atmospheric carbon dioxide concentrations across several ice ages (Sigman and Boyle, 2000; Watson et al., 2000). However, to test the Iron Hypothesis, it was clear that the community would have to design a better experimental approach.

The design of an in situ iron enrichment experiment (mesoscale, i.e., roughly 10 km length scale) required the addition of iron salts dissolved in acidified seawater (not iron filings, as is often reported in the press) and the simultaneous release of a conservative tracer to track the iron-enriched waters (Watson et al., 1991). The tracer chosen was SF_6 (sulfur hexafluoride), which had been used successfully to investigate the physical dynamics of the upper ocean (Ledwell et al., 1993).

In 1993, the first in situ mesoscale iron enrichment—IronEx I—took place in the HNLC waters of the Equatorial Pacific (Martin et al., 1994; see Table 1 for definitions of experiment acronyms). IronEx I was inconclusive because the experiment's iron-enriched and SF_6-labeled 50 km^2 "patch" of water was subducted under a less-dense water body, prematurely ending the study after only a few days (Martin et al., 1994). Nevertheless, it revealed the power of the in situ iron enrichment approach and hinted that Martin's hypothesis (1990) was probably correct. IronEx II, conducted in the same region, confirmed these hints, demonstrating that supplying iron can result in a diatom bloom and that iron plays a fundamental role in many ecological and biogeochemical functions (Coale et al., 1996).

The success of IronEx II paved the way for considering a mesoscale enrichment experiment in the challenging environment of the Southern Ocean (Frost, 1996), which has the largest inventory of unused nutrients in surface waters of any HNLC region (Figure 1). Experiments, commencing with SOIREE (Boyd et al., 2000) and followed by EisenEx (Gervais et al., 2002), SOFeX (Coale et al., 2004), EIFEX (Smetacek et al., 2012), and most recently, LOHAFEX (*Nature Geoscience* editorial, 2009), confirmed that, as in the HNLC waters of the Equatorial Pacific, increased iron supply dramatically alters phytoplankton dynamics, food web structure, and biogeochemical cycles in the Southern Ocean. These major conclusions were also confirmed by the mesoscale experiments SEEDS I (Tsuda et al., 2003), SEEDS II (Tsuda et al., 2007), and SERIES (Boyd et al., 2004) carried out in the third major HNLC region, the sub-Arctic Pacific. In other regions of the ocean, iron and nutrient colimitation has been studied in a joint mesoscale phosphate and iron enrichment experiment, FeeP, in the oligotrophic North Atlantic Ocean (Dixon, 2008).

Boyd et al. (2007) compiled the major

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findings of the many studies conducted in the three HNLC regions. This synthesis revealed that these data sets were a valuable and diverse resource for exploring the links between perturbation of iron supply and the consequent effects on the oceanic carbon cycle, for example, the ratio of photosynthetic carbon fixation per unit of iron added (Boyd et al., 2007). Moreover, such intentional iron enrichment of HNLC waters had additional, and, in some cases, unexpected influences on other biogeochemical cycles, including sulfur, silicon, and nitrogen (e.g., low iron supply increases the silicate demand by diatoms; Hutchins and Bruland, 1998).

These mesoscale experiments were conducted over a more than 15-year period and were each characterized by detailed multidisciplinary studies (see Table 1 and S-Tables 1–3 in Boyd et al., 2007). Thus, each study provided data sets ranging from high-resolution underway sampling (e.g., photosynthetic competence [F_v/F_m]; Behrenfeld et al., 1996) to specialized shipboard experiments, such as the interplay of iron and light on phytoplankton dynamics (Boyd et al., 2000). Taken together, although they were scattered across more than 100 publications, these in situ mesoscale experiments had the potential to supply a wealth of valuable data sets. Furthermore, many of the data sets were unpublished. In 2007 at their Bergen meeting, members of the Scientific Committee on Oceanic Research (SCOR) ratified support for a working group to rescue these data sets and to create a relational database that would be publicly available. This would become WG 131, The Legacy of in situ Iron Enrichment: Data Compilation and Modeling (http://www.scor-int.org/Working_Groups/wg131.htm).

Table 1. The iron enrichment experiments in the SCOR WG 131 data compilation effort are listed along with the FeeP and LOHAFEX projects. References to the experiments are in the text.

Experiment	Voyage Duration	Data Stored	Database	Location
IronEx I	Oct–Nov/1993	Some data	BCO-DMO	5°S, 90°W
IronEx II	May–Jun/1995	Most data	BCO-DMO	4°S, 107°W
SOIREE	Jan–Mar/1999	Most data	BCO-DMO	61°S, 140°E
EisenEx	Oct–Dec/2000	Most data	PANGAEA	48°S, 21°E
SEEDS I	Jun–Aug/2001	Most data	BCO-DMO	48.5°N, 164.5°E
SOFeX-N	Jan–Mar/2002	Most data	BCO-DMO	55°S, 172°W
SOFeX-S	Jan–Mar/2002	Most data	BCO-DMO	66°S, 172°W
SERIES	Jun–Aug/2002	Most data	BCO-DMO	51°N, 144.5°W
EIFEX	Jan–Mar/2004	Many data	PANGAEA	50°S, 2°E
SAGE	Mar–Apr/2004	Most data	BCO-DMO	46.5°S, 172°E
FeeP	Apr–May/2004	Some data	BODC	27.6°N, 22.4°W
SEEDS II	Jul–Aug/2004	Most data	BCO-DMO	48°N, 166°E
LOHAFEX	Feb–Mar/2009	Some data	PANGAEA	48°S, 15°W

BCO-DMO = Biological and Chemical Oceanography Data Management Office
BODC = British Oceanographic Data Centre
EIFEX = European Iron Fertilization Experiment
EisenEx = European Iron Enrichment Experiment
FeeP = Phosphate and Iron Addition Experiment
IronEx I = Iron Experiment I
IronEx II = Iron Experiment II
LOHAFEX = Loha Iron EXperiment (where Loha is Hindi for iron)
PANGAEA = Data Publisher for Earth & Environmental Science
SAGE = Surface-Ocean Lower-Atmosphere Studies Air-Sea Gas Exchange (Experiment)
SEEDS I = Sub-Arctic-Pacific Iron Experiment for Ecosystem Dynamics Study I
SEEDS II = Sub-Arctic Pacific Iron Experiment for Ecosystem Dynamics Study II
SERIES = Sub-Arctic Ecosystem Response to Iron Enrichment Study
SOFeX-N = Southern Ocean Iron Experiment – North
SOFeX-S = Southern Ocean Iron Experiment – South
SOIREE = Southern Ocean Iron Release Experiment

THE RELATIONAL DATABASE

WG 131 members, in partnership with staff at the Biological and Chemical Oceanography Data Management Office (BCO-DMO) at the Woods Hole Oceanographic Institution, compiled data sets from in situ iron enrichment experiments. The resulting database includes detailed information, data, and supporting documentation from nine mesoscale experiments, which represent some of the most challenging and informative experiments undertaken in ocean science. The in situ iron enrichment projects database is part of a larger collection of ocean biogeochemistry data curated by BCO-DMO. The data from nine projects

(IronEx I and II, SOIREE, SOFeX North and South, SERIES, SEEDS I and II, and SAGE [Harvey et al., 2011]) are available directly from the BCO-DMO catalog. Data from the European-led mesoscale experiments aboard R/V *Polarstern* (EisenEx, EIFEX, and soon to be added LOHAFEX) can be accessed via links to the PANGAEA information system (http://www.pangaea.de), hosted by the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven and the Center for Marine Environmental Sciences at the University of Bremen, both in Germany. Finally, data from the FeeP study will be archived at the British Oceanographic Data Centre (http://www.bodc.ac.uk). Please refer to Table 1 for a list of these projects.

In the BCO-DMO data catalog, in situ iron enrichment project data can be accessed readily, as they are grouped together as the Iron Synthesis Program (http://osprey.bco-dmo.org/program.cfm?flag=viewp&id=10&sortby=program). Each project has a separate entry that includes a project description, associated voyage descriptions, and the final quality-assured data sets. The data can be discovered via a text-based interface or by using the map-based, geospatial interface. No login is required and all data are freely available for scholarly use. The data have been reformatted for the database but are otherwise presented as they were contributed by the original investigators. Once discovered in the catalog, data of interest can be viewed in tabular form or as quick-view, user-prepared plots. The BCO-DMO data system supports the ability to browse the catalog using broad categories, including project (e.g., SOIREE), deployment (e.g., COOK19MV), investigator (e.g., Coale), data set (e.g., nitrate), instrument (e.g., CTD), or measurement property name, but the user can also view subsets of the data across different experiments in a variety of ways, such as by measurement name or property ranges. Finally, data of interest can be exported for download in a variety of user-selectable formats.

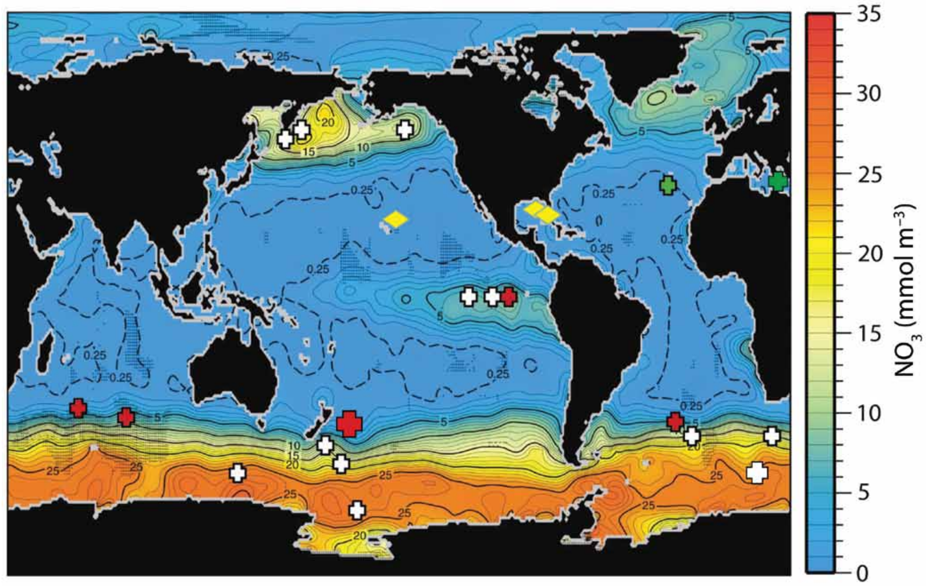

Figure 1. Locations of in situ mesoscale iron enrichment studies (white symbols), iron and/or phosphorous enrichments (green symbols), bloom studies in naturally high iron waters (red symbols), and oceanic geoengineering trials or pilot studies (yellow diamonds), including iron fertilization (Markels and Barber, 2001) and nutrient upwelling using ocean pipes (Lovelock and Rapley, 2007; White et al., 2010). All are overlaid on a map of surface nitrate concentrations for the world ocean. *Nitrate concentrations courtesy of the National Oceanographic Data Centre*

POTENTIAL APPLICATIONS OF THE DATABASE

The SCOR WG 131 relational database is a unique archive of a wide range of interdisciplinary oceanographic data sets from in situ ocean iron enrichment experiments. It is particularly valuable because the future of any further mesoscale in situ iron enrichment experiments is uncertain for several reasons. First, the findings from these experiments have received considerable and selective attention from commercial parties interested in carrying out oceanic geoengineering such that there is confusion, in the popular and scientific press, about whether these studies were conducted for scientific or commercial reasons (see Strong et al., 2009a,b). Second, the Convention on Biological Diversity, negotiated under the auspices of the United Nations Environment Programme and effective since 1993 (http://www.iisd.ca/biodiv/cbdintro.html), implemented a de facto moratorium on future mesoscale iron enrichments of any kind (see Williamson et al., in press, for more details). Thus, it is now very difficult to mount mesoscale iron enrichment studies, as illustrated by the most recent effort, LOHAFEX. This joint Indo-German experiment was ordered not to sail from Capetown by the German government, as it was deemed in contravention of a de facto moratorium on such large-scale manipulation experiments (Schiermeier, 2009). However, two weeks later, the experiment was allowed to proceed (*Nature Geoscience* editorial, 2009).

Here, we provide some examples of how the scope and detail of the SCOR WG 131 relational database can help to significantly advance four emerging research areas. Two of them are directly related to future research into the role of iron biogeochemistry in influencing other biogeochemical cycles, and the other two, ocean geoengineering and the design of studies into submesoscale biogeochemistry, are indirectly related.

Validation of Ocean Biogeochemistry Model Simulations

A wide range of modeling experiments have been conducted in the last 15 years. They include studies to better understand the regional biogeochemistry of HNLC regions, such as the Equatorial Pacific (Chai et al., 2007); global simulations that included mesoscale iron-enriched "patch" experiments (Gnanadesikan et al., 2003; Sarmiento et al., 2010); and site-specific, more-detailed models to investigate iron-mediated processes, such as carbon flow through ecosystems (Denman et al., 2006), carbon export and physical mixing (Boyd et al., 2002), and modes of controls on dimethyl sulfide (DMS) dynamics (Le Clainche et al., 2006). However, few studies have conducted model simulations for each of the three distinct HNLC regions—subpolar, polar, and tropical. With the availability in the relational database of detailed HNLC regional initial conditions—chemical, physical, optical, and biological—prior to enrichment with iron, modelers may be encouraged to undertake HNLC iron enrichment projects, as these data are valuable for both model initialization and later for validation (using different data sets from the relational database). Such a suite of model simulations would provide rigorous validation for models, as the environmental conditions that characterize each region vary considerably among polar, subpolar, and tropical sites, for example, in water temperature and hence algal growth rates (Boyd, 2002), silicate concentrations (Coale et al., 2004), and resident phytoplankton (Silver et al., 2010). The availability of model simulations to test the skill of models across these disparate regions is essential if we are to be able to derive a set of underlying principles with which to demarcate global and regional drivers of the functioning of HNLC regions.

Understanding the Interplay of Biogeochemical Cycles and Ecosystem Food Webs

The large areal extent of in situ iron enrichments provides a unique opportunity to assess the response of pelagic ecosystems, from microbes to macrozooplankton, to purposeful stimulation of phytoplankton growth. The concurrent sampling of a broad suite of both food web and biogeochemical properties enables unprecedented exploration of the links between shifts in flora and fauna and the biogeochemical cycles of a range of elements. This relational database provides a useful testbed for exploring and developing mechanistic links between ecology and biogeochemistry. There are many examples within the relational database (one of which is highlighted in Figure 2) that detail how iron-mediated increases in the abundances of particular phytoplankton groups in HNLC waters result in shifts in the dominant microzooplankton community. These changes in flora and fauna result in marked alteration of sulfur biogeochemistry. Specifically, as shown in Figure 2, there is a pronounced increase in the abundance of phytoflagellates, a group that produces intracellular DMSPp (particulate dimethylsulfonioproprionate). The phytoflagellates increase in abundance until there is a shift in the microzooplankton community from small heterotrophic flagellates to larger ciliates. The ciliates graze on the phytoflagellates, resulting in a release of DMSP that is converted to DMS (Turner et al., 2004).

Moreover, such a holistic view of the interplay of bottom-up environmental versus top-down ecological shifts in controlling biota provides valuable insight into the extent, and on which timescales, ecosystems may be altered by another, more complex, environmental perturbation—climate change. This broad view will help us better understand how climate change-mediated shifts in ecosystem structure and function will feed back biogeochemically to climate change (Legendre and Rivkin, 2005; Boyd et al., 2010).

Understanding the Issues and Implications of Geoengineering

In the last five years, a growing literature has explored a range of potential geoengineering methods (Markels and Barber, 2001; Lovelock and Rapley, 2007; Boyd, 2008; Shepherd et al., 2009; White et al., 2010; Russell et al., 2012). However, data from pilot studies or trials are scarce (Figure 1), and it is thus difficult to make progress on this important debate (Russell et al., 2012). There have been three ocean trials (Figure 1), only one of which has been published in the peer-reviewed literature. In situ mesoscale iron enrichments, although carried out for very different reasons than that of geoengineering (Strong et al., 2009a,b), nevertheless represent an important asset. These mesoscale, multidisciplinary experiments can provide insights into key outcomes of oceanic perturbations, such as their efficacy, side effects, safety, unknowns, and unanticipated results, that can be used to inform the ongoing debate about geoengineering methods (Boyd, 2008). Such data sets also highlight the limitations of even these large-scale carefully monitored perturbations of the planet, as they could not provide sufficient data to fully inform the geoengineering debate (Watson et al., 2008).

A Primer for Submesoscale Biogeochemistry Studies

A growing interest in the study of biogeochemistry at relatively small (0–10 km) scales (Lévy et al., 2012) has followed the significant findings about how ocean physics varies at the submesoscale (see references in Lévy et al., 2012). However, to date, many studies have had limited success in linking submesoscale physics to chemistry, then to biology, and eventually to biogeochemical processes, such as export downward flux (Guidi et al., 2009; Resplandy et al., 2012). Issues that need to be better addressed include defining the temporal sampling resolution needed to resolve submesoscale processes and improving understanding of the timescales of related changes in physics, chemistry, and biology. For example, what is the timescale of episodic nutrient supply in response to transient submesoscale physical forcing, and how does it influence the consequent response times of biota?

Mesoscale iron enrichment experiments can offer useful insights into and constraints on how best to study submesoscale biogeochemistry because the timing of a mesoscale nutrient pulse (i.e., iron enrichment) is strictly controlled. Moreover, the subsequent effects of the nutrient pulse on the resident biota and, consequently, on biogeochemical fluxes, are tracked, often using high-resolution (i.e., minutes) underway sampling (e.g., fast repetition rate fluorometry; Behrenfeld et al., 1996; Boyd et al., 2000). These experiments are also characterized by a suite of interdisciplinary techniques that can provide useful information on the submesoscale, including how biological or food web responses to iron enrichment manifest themselves, the timescales over which these responses become detectable, and how such biological responses vary regionally (e.g., due to differences in water temperatures and, hence, physiological rates among polar, subpolar, and tropical HNLC waters). Together, these mesoscale iron-enrichment data sets offer guidance on which properties or proxies provide the best metrics for the detection and attribution of shifts in biological processes resulting from transient shifts in the physics and chemistry (Figure 3). The relational database of in situ iron enrichments also provides information on the subsequent timescales of altered ecosystem function, and its consequent effect on biogeochemistry and on important processes such as downward export flux.

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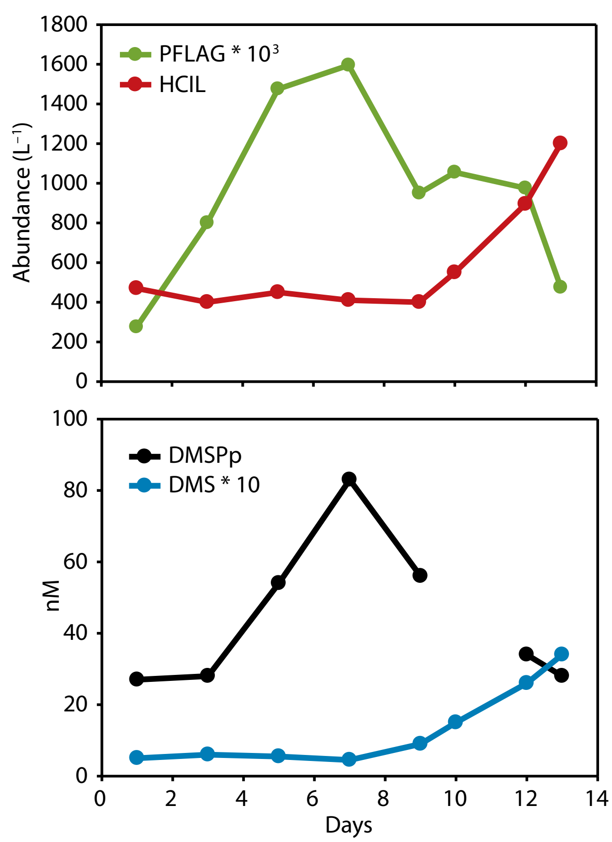

Figure 2. An example of the indirect effects of iron enrichment (on day zero) on food web structure and the consequent effects on sulfur biogeochemistry. A faunistic shift to large microzooplankton (heterotrophic ciliates, denoted by HCIL, upper panel) occurs in response to iron-mediated increases in phytoflagellate abundances (denoted by PFLAG, upper panel). The increase in phytoflagellate abundances leads to a buildup of DMSPp (particulate dimethylsulfonioproprionate, lower panel) concentrations, and then to grazer-mediated release of the DMSPp and conversion to the climate-reactive gas DMS (dimethyl sulfide, lower panel). Data are from the SOIREE experiment, and are available from the BCO-DMO relational database.

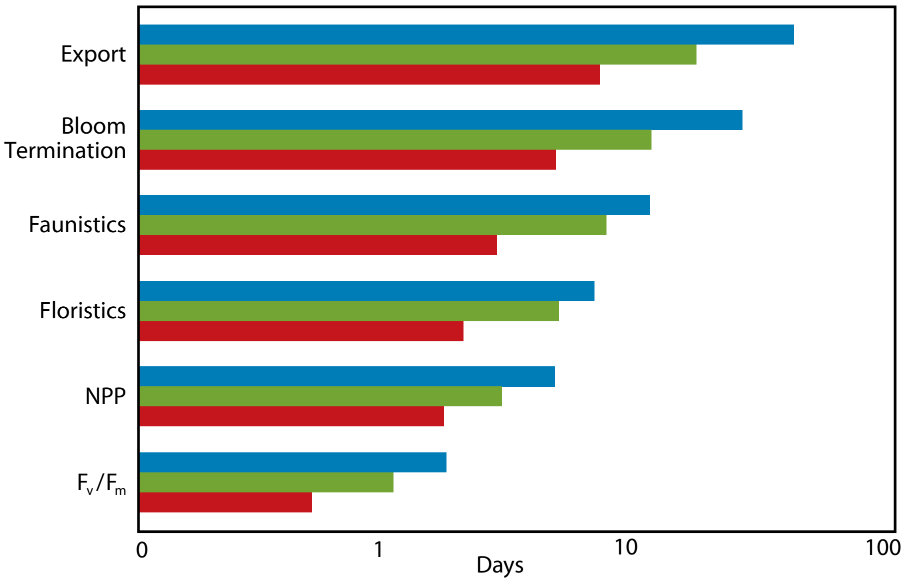

Figure 3. A summary of the timescales of biological responses (log time scale, 0 denotes iron release), from photosynthetic to biogeochemical, following purposeful mesoscale iron enrichment. F_v/F_m is phytoplankton photosynthetic competence; NPP denotes Net Primary Production. See Figure 2 for examples of shifts in flora and fauna. Bloom termination is defined as the period during which a sustained decrease in bloom stocks is observed. Export is defined as enhancement of the downward flux of particles in the upper 300 m. The temporal trends demonstrate that different locales have characteristic response times (red denotes tropical HNLC [high nutrient low chlorophyll] waters; green, subpolar HNLC waters; blue, polar HNLC waters). Data are available from the BCO-DMO relational database.

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REFERENCES

Banse, K. 1991. Rates of phytoplankton cell division in the field and in iron enrichment experiments. *Limnology and Oceanography* 36(8):1,886–1,898.

Behrenfeld, M.J., A.J. Bale, Z.S. Kolber, J. Aiken, and P.G. Falkowski. 1996. Confirmation of iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean. *Nature* 383:508–513, http://dx.doi.org/10.1038/383508a0.

Boyd, P.W., A.J. Watson, C.S. Law, E.R. Abraham, T. Trull, R. Murdoch, D.C.E. Bakker, A.R. Bowie, K.O. Buesseler, H. Chang, and others. 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. *Nature* 407:695–702, http://dx.doi.org/10.1038/35037500.

Boyd, P.W. 2002. The role of iron in the biogeochemistry of the Southern Ocean and equatorial Pacific: A comparison of in situ iron enrichments. *Deep-Sea Research Part II* 49:1,803–1,821, http://dx.doi.org/10.1016/S0967-0645(02)00013-9.

Boyd, P.W., G.A. Jackson, and A.M. Waite. 2002. Are mesoscale perturbation experiments in polar waters prone to physical artefacts? Evidence from algal aggregation modelling studies. *Geophysical Research Letters* 29(11), 1541, http://dx.doi.org/10.1029/2001GL014210.

Boyd, P.W., T. Jickells, C.S. Law, S. Blain, E.A. Boyle, K.O. Buesseler, K.H. Coale, J.J. Cullen, H.J.W. de Baar, M. Follows, and others. 2007. Mesoscale iron enrichment experiments 1993–2005: Synthesis and future directions. *Science* 315:612–617, http://dx.doi.org/10.1126/science.1131669.

Boyd, P.W., C.S. Law, C.S. Wong, Y. Nojiri, A. Tsuda, M. Levasseur, S. Takeda, R. Rivkin, P.J. Harrison, R. Strzepek, and others. 2004. The decline and fate of an iron-induced subarctic phytoplankton bloom. *Nature* 428(6982):549–553, http://dx.doi.org/10.1038/nature02437.

Boyd, P.W., E. Ibisanmi, S.G. Sander, K.A. Hunter, and G.A. Jackson. 2010. Remineralization of upper ocean particles: Implications for iron biogeochemistry. *Limnology and Oceanography* 55(3):1,271–1,288, http://dx.doi.org/10.4319/lo.2010.55.3.1271.

Boyd, P.W. 2008. Ranking geo-engineering schemes. *Nature Geoscience* 1:722–724, http://dx.doi.org/10.1038/ngeo348.

Chai, F., M.S. Jiang, Y. Chao, R.C. Dugdale, F. Chavez, and R.T. Barber. 2007. Modeling responses of diatom productivity and biogenic silica export to iron enrichment in the equatorial Pacific Ocean. *Global Biogeochemical Cycles* 21, GB3S90, http://dx.doi.org/10.1029/2006GB002804.

Chisholm, S.W., and F.M.M. Morel, eds. 1991. What controls phytoplankton production in nutrient-rich areas of the open sea? *Limnology and Oceanography* 36(8):1,507–1,970.

Coale, K.H., K.S. Johnson, S.E. Fitzwater, R.M. Gordon, S. Tanner, F.P. Chavez, L. Ferioli, C. Sakamoto, P. Rogers, F. Millero, and others. 1996. A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* 383:495–511, http://dx.doi.org/10.1038/383495a0.

Coale, K.H., K.S. Johnson, F.P. Chavez, K.O. Buesseler, R.T. Barber, M.A. Brzezinski, W.P. Cochlan, F.J. Millero, P.G. Falkowski, J.E. Bauer, and others. 2004. Southern Ocean iron enrichment experiment: Carbon cycling in high- and low-Si waters. *Science* 304:408–414, http://dx.doi.org/10.1126/science.1089778.

De Baar, H.J.W. 1994. Von Liebig's Law of the Minimum and plankton ecology (1899–1991). *Progress in Oceanography* 33:347–386, http://dx.doi.org/10.1016/0079-6611(94)90022-1.

Denman, K.L., C. Völker, M.A. Peña, and R.B. Rivkin. 2006. Modelling the ecosystem response to iron fertilization in the subarctic NE Pacific: The influence of grazing, and Si and N cycling on CO_2 drawdown. *Deep-Sea Research Part II* 53:2,327–2,352, http://dx.doi.org/10.1016/j.dsr2.2006.05.026.

Dixon, J.L. 2008. Macro and micro nutrient limitation of microbial productivity in oligotrophic subtropical Atlantic waters. *Environmental Chemistry* 5:135–142, http://dx.doi.org/10.1071/EN07081.

Frost, B.W. 1996. Phytoplankton bloom on iron rations. *Nature* 383:474–476, http://dx.doi.org/10.1038/383475a0.

Gervais, F., U. Riebesell, and M.Y. Gorbunov. 2002. Changes in primary productivity and chlorophyll *a* in response to iron fertilization in the southern Polar Frontal Zone. *Limnology and Oceanography* 47:1,324–1,335.

Gnanadesikan, A., J.L. Sarmiento, and R.D. Slater. 2003. Effects of patchy ocean fertilization on atmospheric carbon dioxide and biological production. *Global Biogeochemical Cycles* 17(2), 1050, http://dx.doi.org/10.1029/2002GB001940.

Guidi, L., P.H.R. Calil, S. Duhamel, K.M. Björkman, S.C. Doney, G.A. Jackson, B. Li, M.J. Church, S. Tozzi, Z.S. Kolber, and others. 2009. Does eddy-eddy interaction control surface phytoplankton distribution and carbon export in the North Pacific Subtropical Gyre? *Journal of Geophysical Research* 117, G02024, http://dx.doi.org/10.1029/2012JG001984.

Hart, T.J. 1934. On the phytoplankton of the Southwest Atlantic and the Bellingshausen Sea 1929–1931. *Discovery Reports* 8:1–268.

Harvey, M.J., C.S. Law, M.J. Smith, J.A. Hall, E.R. Abraham, C.L. Stevens, M.G. Hadfield, D.T. Ho, B. Ward, S.D.Archer, and others. 2010. The SOLAS air–sea gas exchange experiment (SAGE) 2004. *Deep-Sea Research Part II* 58:753–763, http://dx.doi.org/10.1016/j.dsr2.2010.10.015.

Hutchins, D.A., and K.W. Bruland. 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. *Nature* 393:561–564, http://dx.doi.org/10.1038/31203.

Le Clainche, Y., M. Levasseur, A. Vezina, R.-C. Bouillon, A. Merzouk, S. Michaud, M. Scarratt, C.S. Wong, R.B. Rivkin, P.W. Boyd, and others. 2006. Modeling analysis of the effect of iron enrichment on dimethyl sulfide dynamics in the NE Pacific (SERIES experiment). *Journal of Geophysical Research* 111, C01011, http://dx.doi.org/10.1029/2005JC002947.

Ledwell, J.R., A.J. Watson, and C.S. Law. 1993. Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment. *Nature* 364:701–703, http://dx.doi.org/10.1038/364701a0.

Legendre, L., and R.B. Rivkin. 2005. Integrating functional diversity, food web processes, and biogeochemical carbon fluxes into a conceptual approach for modelling the upper ocean in a high-CO_2 world. *Journal of Geophysical Research* 111, C09S17, http://dx.doi.org/10.1029/2004JC002530.

Lévy, M., R. Ferrari, P.J.S. Franks, A.P. Martin, and P. Rivière. 2012. Bringing physics to life at the submesoscale. *Geophysical Research Letters* 39, L14602, http://dx.doi.org/10.1029/2012GL052756.

Lovelock, J.E., and C.G. Rapley. 2007. Ocean pipes could help the Earth to cure itself. *Nature* 449:403, http://dx.doi.org/10.1038/449403a.

Markels, M. Jr., and R.T. Barber. 2001. Sequestration of carbon dioxide by ocean fertilization. Paper presented at the 1st National Conference on Carbon Sequestration, National Energy and Technology Laboratory, Washington, DC, May 14–17, 2001.

Martin, J.H., and S.E. Fitzwater. 1988. Iron deficiency limits phytoplankton growth in the northeast Pacific subarctic. *Nature* 331:341–343, http://dx.doi.org/10.1038/331341a0.

Martin, J.M. 1990. Glacial-interglacial CO_2 change: The iron hypothesis. *Paleoceanography* 5:1–13, http://dx.doi.org/10.1029/PA005i001p00001.

Martin, J.M., K.H. Coale, K.S. Johnson, S.E. Fitzwater, R.M. Gordon, S.J. Tanner, C.N. Hunter, V.A. Elrod, J.L. Nowicki, T.L. Coley, and others. 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 371:123–129, http://dx.doi.org/10.1038/371123a0.

Nature Geoscience editorial. 2009. The Law of the Sea. *Nature Geoscience* 2:153, http://dx.doi.org/10.1038/ngeo464.

Resplandy, L., A.P. Martin, F. LeMoigne, P. Martin, A. Aquilina, L. Mémery, M. Lévy, and R. Sanders. 2012. How does dynamical spatial variability impact ^{234}Th-derived estimates of organic export? *Deep-Sea Research Part I* 68:24–45, http://dx.doi.org/10.1016/j.dsr.2012.05.015.

Russell, L.M., P.J. Rasch, G.M. Mace, R.B. Jackson, J. Shepherd, P. Liss, M. Leinen, D. Schimel, N.E. Vaughan, A.C. Janetos, and others. 2012. Ecosystem impacts of geoengineering: A review for developing a science plan. *Ambio* 41(4):350–369, http://dx.doi.org/10.1007/s13280-012-0258-5.

Sarmiento, J.L., R.D. Slater, J. Dunne, A. Gnanadesikan, and M.R. Hiscock. 2010. Efficiency of small scale carbon mitigation by patch iron fertilization. *Biogeosciences* 7:3,593–3,624, http://dx.doi.org/10.5194/bg-7-3593-2010.

Schiermeier, Q. 2009. Ocean fertilization experiment suspended. *Nature*, http://dx.doi.org/10.1038/news.2009.26.

Shepherd, J., K. Caldeira, P. Cox, J. Haigh, D. Keith, B. Launder, G. Mace, G. MacKerron, J. Pyle, S. Rayner, and others. 2009. Geoengineering the climate: Science, governance and uncertainty. *Royal Society Policy Document* 10/09, 81 pp.

Sigman, D.M., and E.A. Boyle. 2000. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* 407:859–869, http://dx.doi.org/10.1038/35038000.

Silver, M.W., S. Bargu, S.L. Coale, C.R. Benitez-Nelson, A.C. Garcia, K.J. Roberts, E. Sekula-Wood, K.W. Bruland, and K.H. Coale. 2010. Toxic diatoms and domoic acid in natural and iron enriched waters of the oceanic Pacific. *Proceedings of the National Academy of Sciences of the United States of America* 107(48):20,762–20,767, http://dx.doi.org/10.1073/pnas.1006968107.

Smetacek, V., C. Klaas, V. Strass, P. Assmy, M. Montresor, B. Cisewski, N. Savoye, A. Webb, F. d'Ovidio, J.M. Arrieta, and others. 2012. Deep carbon export from a Southern Ocean iron-fertilized diatom bloom. *Nature* 478(7407):313–319, http://dx.doi.org/10.1038/nature11229.

Strong, A.L., S.W. Chisholm, C. Miller, and J. Cullen. 2009a. Ocean fertilization: Time to move on. *Nature* 361:347–348, http://dx.doi.org/10.1038/461347a.

Strong, A.L., J.J. Cullen, and S.W. Chisholm. 2009. Ocean fertilization: Science, policy, and commerce. *Oceanography* 22(3):236–261, http://dx.doi.org/10.5670/oceanog.2009.83.

Tsuda, A., S. Takeda, H. Saito, J. Nishioka, I. Kudo, Y. Nojiri, K. Suzuki, M. Uematsu, M.L. Wells, D. Tsumune, and others. 2007. Evidence for the grazing hypothesis: Grazing reduces phytoplankton responses of the HNLC ecosystem to iron enrichment in the western subarctic Pacific (SEEDS II). *Journal of Oceanography* 63:983–994, http://dx.doi.org/10.1007/s10872-007-0082-x.

Tsuda, A., S. Takeda, H. Saito, J. Nishioka, Y. Nojiri, I. Kudo, H. Kiyosawa, A. Shiomoto, K. Imai, T. Ono, and others. 2003. A mesoscale iron enrichment in the western Subarctic Pacific induces a large centric diatom bloom. *Science* 300:958–961, http://dx.doi.org/10.1126/science.1082000.

Turner, S.M., M.J. Harvey, C.S. Law, P.D. Nightingale, and P.S. Liss. 2004. Iron-induced changes in oceanic sulfur biogeochemistry. *Geophysical Research Letters* 31, L14307, http://dx.doi.org/10.1029/2004GL020296.

Watson, A.J., P.S. Liss, and R.A. Duce, 1991. Design of a small-scale in situ iron fertilization experiment. *Limnology and Oceanography* 36:1,960–1,965.

Watson, A.J., D.C.E. Bakker, P.W. Boyd, A.J. Ridgwell, and C.S. Law. 2000. Effect of iron supply on Southern Ocean CO_2 uptake and implications for glacial atmospheric CO_2. *Nature* 407:730–733, http://dx.doi.org/10.1038/35037561.

Watson, A.J., P.W. Boyd, S. Turner, T. Jickells, and P. Liss. 2008. Designing the next generation of ocean iron fertilization experiments. *Marine Ecology Progress Series* 364:303–309, http://dx.doi.org/10.3354/meps07552.

White, A., K. Björkman, E. Grabowski, R. Letelier, S. Poulos, B. Watkins, and D. Karl. 2010. An open ocean trial of controlled upwelling using wave pump technology. *Journal of Atmospheric and Oceanic Technology* 27:385–396, http://dx.doi.org/10.1175/2009JTECHO679.1.

Williamson, P., D.W.R. Wallace, C.S. Law, P.W. Boyd, Y. Collos, P. Croot, K. Denman, U. Riebesell, S. Takeda, and C. Vivian. In press. Ocean fertilization for geoengineering: A review of effectiveness, environmental impacts and emerging governance. *Process Safety and Environmental Protection*, http://dx.doi.org/10.1016/j.psep.2012.10.007.