Increasing Oceanic Carbon Fixation Through Fe Fertilization: Opportunity for Mine Water?

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Abstract Approximately 30 % of the Earth's oceans support low rates of primary production because of low Fe concentrations. The fertilization of these waters with Fe has been proposed as a tool for creating phytoplankton blooms, increasing carbon fixation, and sequestering carbon in deep ocean waters. This paper reviews the status of the ocean iron fertilization (OIF) concept and assesses the opportunity it may provide to mining companies and mine water professionals who regularly deal with large quantities of Fe. Using data produced by large OIF experiments, calculations are provided regarding the efficiency of Fe additions for carbon fixation and the quantities of Fe that would be needed if OIF became an accepted practice. The gross value of Fe used in OIF projects is calculated from the current value of carbon credits and salmon and tuna fisheries. If the OIF concept advances, the huge demand for Fe that will be created may justify reconsideration of mine water treatment practices that produce more pure Fe solids than is the case with conventional treatment technologies.

Keywords Iron · Phytoplankton · Carbon sequestration · Mine water · OIF

Introduction

Concentrations of dissolved Fe on Earth range over ten orders of magnitude. The highest Fe concentrations are typically measured in mine waters where values commonly exceed 100 mg/L and can range above 100,000 mg/L

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(Nordstrom et al. 2000). The lowest Fe concentrations generally occur in oceans where values <0.1 µg/L are common and a value of 0.009 µg/L was measured in the Southern Ocean (Martin 1990). Fe is ecologically important at both ends of the concentration spectrum. Excessive Fe concentrations are devastating to receiving water bodies because of its effect on dissolved oxygen, pH, and turbidity, while low Fe concentrations are ecologically important because the metal is a micronutrient used by phytoplankton, cyanobacteria, and bacteria for fixing atmospheric nitrogen, reducing nitrate, and chlorophyll synthesis (Martin 1990). In many oceanic waters that contain high concentrations of major nutrients, primary productivity is limited to very low rates by Fe deficiency. Because Fe's involvement in photosynthesis is enzymatic, a small addition of Fe can result is a very large increase in primary production (Morel et al. 1991). In laboratory studies of Fe-starved phytoplankton cultures, additions of 1 g of dissolved Fe were found to result in 30,000–100,000 g of C fixation (Buesseler and Boyd 2003).

The oceanographer John Martin first recognized the role of Fe in regulating marine primary productivity and proposed that the relationship was large enough to affect global climate (Martin 1990). Martin hypothesized that during the last glacial maxima, aerosol Fe concentrations were 50 times higher than currently exist because of increased wind-driven erosion of bare landmasses associated with expanded glaciation. The large input of Fe to the oceans would have substantially increased primary productivity. Phytoplankton that sank to the ocean floor resulted in long-term transfer of C from the atmosphere to ocean sediments. Martin's hypothesis has recently been confirmed by studies of Antarctic ice cores showing increased dust deposition to the Southern Ocean during

glacial periods (Lamy et al. 2014) and increased plankton growth during periods with elevated dust and Fe (Jickells et al. 2005; Martinez-Garcia et al. 2014).

Martin also acknowledged the possibility of Fe fertilization as a geoengineering option to increase oceanic primary productivity and sequester a portion of the carbon fixation into ocean sediments, thus affecting atmospheric CO_2 concentrations. Recent CO_2 sequestration interests have raised the profile of the Fe fertilization concept and several large fertilization experiments have occurred. Because mine water professionals commonly deal with large excesses of Fe, the purpose of this paper was to review the Fe fertilization literature and assess the opportunity for mine water or mine water solids to participate in future Fe fertilization efforts.

Ocean Iron Fertilization Experiments

To date, 13 ocean iron fertilization (OIF) experiments have been reported in the peer-reviewed literature (Boyd et al. 2007; Smetacek et al. 2012). In most experiments, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was dissolved in acidified sea water and discharged into the ocean surface through the propeller wake of the research vessel. The quantity of iron added ranged from 350 to 2,820 kg of Fe applied over tens or hundreds of km^2 of ocean. These amounts of Fe are quite small relative to the volume of water impacted, constituting no more than 0.06 g/m^2 of ocean surface and resulting in Fe concentrations in the surface waters no more than 10 μg/L.

Recent OIF experiments have been carried out in eddies because they can be identified by satellites and the waters inside and outside an eddy, to a large extent, do not mix. This allows for comparison between fertilized and unfertilized conditions over a small area where other environmental conditions are similar. Monitoring of fertilized and unfertilized waters has occurred over periods ranging from a few days to 5 weeks. The parameters monitored include, at a minimum: chlorophyll, nitrate, phosphate, silica, Fe, dissolved inorganic carbon, particulate organic carbon, and dominant phytoplankton and zooplankton (Boyd et al. 2007).

In most marine environments, primary production is limited by nitrate concentrations. However, some ocean surface waters contain high concentrations of nitrate but are still unproductive. These waters also contain low concentrations of chlorophyll (an easily measured surrogate for planktonic abundance) and are referred to as "high nitrate, low chlorophyll" or HNLC. Figure 1 shows oceanic nitrate concentrations. Approximately one-third of the oceans are HNLC (Boyd 2004). HNLC areas can exist for a variety of reasons including lack of sunlight and low

concentrations of phosphate or micronutrients. The largest HNLC areas are in the Southern Ocean and northern Pacific Ocean. In these high latitude areas, primary production is limited by sunlight in winter months and by Fe in summer months. Unused surface macronutrients are returned by ocean currents to depths where they are unavailable for photosynthetic activity for decades or centuries. While the largest HNLC areas are in high latitude waters, moderate HNLC areas exist in the eastern Pacific between the equator and 20°S latitude.

Ocean iron fertilization experiments have conclusively demonstrated that Fe addition to HNLC waters produces plankton blooms and increases chlorophyll and primary productivity. The composition of the plankton bloom and the fate of the fixed carbon are both related to silicon (Si) concentrations. In Si-rich waters, diatoms (single cell phytoplankton with a cell wall made of silica) are typically dominant. Diatoms are not heavily grazed (their silica armoring lessens predation) and when they die, they can sink to the deep ocean. These characteristics make diatom-dominated blooms good targets for carbon sequestration projects. In Si-deficient waters, non-siliceous phytoplankton are usually dominant. These plankton are heavily grazed by zooplankton and copepods and thus contribute carbon to the local marine food chain. The SOFEX OIF project conducted simultaneous Fe fertilization experiments in Si-deficient and Si-rich portions of the Southern Ocean in 2002 (Coale et al. 2004). Both fertilizations resulted in large phytoplankton blooms. Diatoms dominated the bloom in Si-rich waters and a portion of the bloom settled to the ocean floor. The Si-deficient bloom was equal in size but compositionally different. Half of the bloom consisted of non-siliceous plankton that were heavily grazed with little export of carbon to the ocean floor. A similar result was reported by a 2009 OIF in a Si-deficient portion of the south-western Atlantic where a non-diatom phytoplankton bloom was followed by a zooplankton bloom that kept the phytoplankton population in check (Mazzocchi et al. 2009).

EIFEX Project

The most detailed OIF experiment to date was the European Iron Fertilization Experiment (EIFEX), which was conducted in the Southern Ocean in summer 2004 (Smetacek et al. 2012). 2,820 kg of Fe was injected into the ocean water and the fertilized and unfertilized areas were monitored for 37 days. The fertilization increased Fe concentrations in the target area by 0.084 μg/L. A large diatom-dominated plankton bloom occurred in the fertilized patch. Concentrations of nitrate, dissolved inorganic carbon, and silicate decreased inside the fertilized patch yet remained stable outside the patch. Concentrations of

chlorophyll, particulate organic carbon, particulate organic nitrogen and biogenic silica all increased inside the fertilized patch yet remained stable outside. A fivefold increase in chlorophyll was primarily due the growth of large diatoms. Silicate concentrations in the surface water decreased during the experiment but not to levels limiting diatom growth. The bloom was ongoing when the experiment was terminated.

In addition to documenting surface conditions, the EIFEX team measured particulate organic carbon concentrations at various depths below the bloom in order to assess the sinking and possible sequestration of carbon. 24 days after initial fertilization, particulate organic carbon stocks increased sharply below a depth of 200 m as diatoms died en masse and formed sinking aggregates. Increases in particulate organic carbon from 300 to 3,000 m were accompanied by decreases near the surface (Smetacek et al. 2012).

Fe fertilization doubled primary productivity and increased C fixation by phytoplankton in the surface water by 2.4 mol/m^2. The mass ratio of increased C-fixation to Fe addition was 2,857. Each gram of Fe added resulted in 2,857 g of C fixation by plankton. This ratio is an underestimate because chlorophyll concentrations inside the patch were still elevated when the monitoring ceased. 50 % of the

increased C fixation, or 1.2 mol/m^2, sank below 1,000 m, which is considered sequestered by most marine scientists. The mass ratio of C sequestration to Fe addition was 1,434.

Geoengineering

The results of all OIF experiments to date indicate that Fe fertilization of HNLC ocean waters initiates a phytoplankton bloom that increases primary production. If the bloom is dominated by diatoms, a significant portion of the fixed C can settle to the ocean floor and be considered sequestered. Blooms dominated by non-siliceous phytoplankton are heavily grazed and do not provide sequestration benefits. Instead, the fixed C is incorporated into the food chain and potentially increases the productivity of the location marine ecosystem. We will present rough calculations that explore sequestering carbon and increasing productivity on a large scale.

The following calculations (Table 1) draw on data produced by the EIFIX project. The EIFEX project increased C fixation by phytoplankton by 28.8 g/m^2 of ocean surface. If the entire Southern Ocean was fertilized (one event), the resulting increase in C fixation would be 585 million tonnes (t). Approximately 30 % of the Southern Ocean contains Si concentrations high enough to
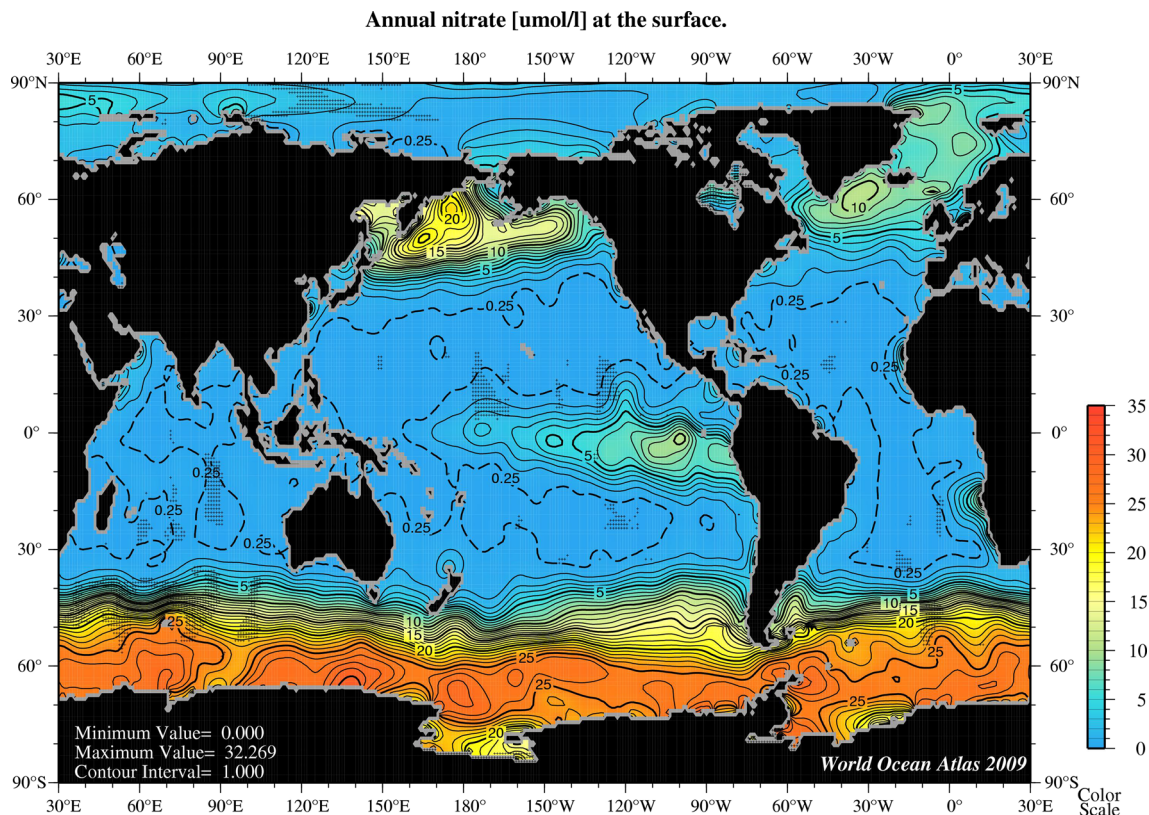

Fig. 1 Oceanic concentrations of nitrate in μmol/L (Garcia et al. 2010)

Table 1 Carbon sequestration potential of the Southern Ocean

	Value	Source
Fe induced C fixation	28.8 g C/m^2	Smetacek et al. (2012)
Area of Southern Ocean	20.3 million km^2	www.worldatlas.com
Carbon fixation potential for Southern Ocean (one event)	585 million t of C	Calculation
Percentage of Southern Ocean with high Si	30 %	Smetacek et al. (2012)
Sequestration of C in in high Si areas	14.4 g C/m^2	Smetacek et al. (2012)
Carbon sequestration potential Southern Ocean (one event)	88 million t of C	Calculation
C fixation: Fe fertilization, mass ratio	2,857:1	Smetacek et al. (2012)
Fe fertilization requirement per event	205,000 t Fe	Calculation

support a diatom bloom (Coale et al. 2004). If half of the C fixed in the diatom blooms sank to the ocean floor, the total C sequestration would be 88 million t. For context, the total C emissions from fuel combustion in 2010 were approximately 8.3 billion t (IEA 2012). The once/year event presented in Table 1 could theoretically sequester enough carbon to offset 1 % of the annual fuel combustion C emissions.

Table 1 shows the amount (207,000 t) of Fe needed to support a one-time fertilization of the Southern Ocean at the EIFEX project rate. The actual amount of Fe required depends on the purity of the source. If $FeSO_4 \cdot 7H_2O$ was used, 1,035,000 t would be required.

Value of OIF

The value of large OIF efforts depends on the values of sequestered carbon and increased ocean productivity. The value of carbon sequestration can be estimated from carbon credit markets. The primary carbon credit market is the European Union Emission Trading System (EU ETS) where, in 2013, credits for 570 mtonC were traded at an average value of $1.76/mtonC (Newell et al. 2014). Secondary markets are developing. In 2013, the Regional Greenhouse Gas Initiative sold credits for 45 mtonC at an average price of $0.80/mtonC (Newell et al. 2014) and the California Cap and Trade system sold credits for 44 mtonC for $3.19/mtonC (California EPA 2013). Based on the EU ETS value, the gross value of C sequestration by the EIFIX project was $25/km^2. The sequestration value of the Southern Ocean event considered in Table 1 is estimated at $152 million.

Fe fertilization of Si-deficient ocean waters also stimulates the marine ecosystem. The EIFIX project reported an increase in gross primary production of 28.8 gC/m^2 and 2,857 units C per unit Fe injected. Assuming that C flows through marine ecosystems similar to energy, then 10 % of the C is expected to transfer between each trophic level (Odum 1988). For a five trophic level food chain (typical of salmon or tuna), the transfer rate of C from phytoplankton to the top carnivore is 10^{-4}. The C content of top carnivore (salmon, tuna) is approximately 11 % of fresh weight. If none of the C fixation is lost to sequestration, then each km^2 of Southern Ocean produces an additional 26 kg (freshweight) of top predator. The Southern Ocean, under the conditions in Table 1, produces an additional 364,000 t of top predator.

The value of the additional production was estimated from the value of salmon and tuna. In 2013, the wholesale price for whole salmon captured in the north Pacific was approximately $8.80/kg. The wholesale price for whole Pacific yellow fin tuna was approximately $10.36/kg. Using an average value of $9.58/kg, the gross fishery value of the Fe fertilization (with no loss to sequestration) is $245/km^2, $24,331/t of Fe injected, and $3.5 billion for the Southern Ocean. The realized value of the fishery enhancement depends on the catch rate. Assuming a 50 % catch rate (personal communication, Carl Walters, University of British Columbia Fisheries Centre), yields realized gross values for the Fe fertilization of $123/km^2 and $1.7 billion for the Southern Ocean.

Table 2 compares the calculated values of the Fe injections into the Southern Ocean with varying Si concentrations. In Si-deficient waters, all the C-fixation is captured by the food chain. The resulting increase in fishery values is $12,167/t of Fe. In Si-rich waters, diatoms dominate and 50 % of the C sinks to the deep ocean and provides sequestration benefits. The remaining C-fixation is incorporated into the local food chain and provides fishery benefits. The combined fishery and sequestration values are $8,597/t of Fe. This analysis suggests a gross value of $8,000–11,000/t Fe.

Sourcing Fe for OIF from Mine Water

The primary source of Fe for OIF projects has been $FeSO_4 \cdot 7H_2O$, which has a current bulk wholesale cost of approximately $100/t. Fe accounts for 20 % of the $FeSO_4 \cdot 7H_2O$ molecule, so the cost of Fe is approximately $500/t of Fe. $FeSO_4 \cdot 7H_2O$ is produced as a by-product of steel and titanium manufacturing and is available in large quantities.

The large difference between the cost of Fe ($500/t) and the potential OIF value of a tonne of Fe ($8,000–11,000/t) should not be interpreted as the potential profitability of the concept. The process of delivering Fe to a HNLC ocean

Table 2 Consequences of 1 tonne Fe fertilization in Southern Ocean in low and high Si waters

	Si-deficient	Si-rich	
	Fe, 1000 kg ↓	Fe, 1000 kg	Sink to deep ocean
1° Productivity	2,857,286 kg C	1,428,643 kg C	1,428,643 kg C
2° grazer	285,729 kg C	142,864 kg C	
3° predator	28,573 kg C	14,286 kg C	
4° predator	2,857 kg C	1,429 kg C	
5° predator	286 kg C	143 kg C	
5° Biomass*	2,540 kg	1,270 kg	
Catch rate	50%	50%	
Biomass value	$9.58/kg	$9.58/kg	
Carbon value**			$1.76/t
OIF value	$12,1675	$6,083	$2,514

Carbon calculations based on results of EIFAX (Smetacek et al. 2012)

[a] Top predator is 11 % C, fresh weight

[b] European Union Emission Trading System 2013

Table 3 Composition of solids (in %, unless otherwise stated) produced by various coal mine drainage treatment techniques (Hedin 2012)

Site	Water chemistry		Treatment solids chemistry						
	pH	Fe (mg/L)	Si	Al	Fe	Mn	Mg	Ca	Cu (ppm)
Lime treatment									
Man	3.3	247	2.1	2.5	27.8	0.3	1.5	13.4	24
Cul	6.1	67	2.4	0.6	10.5	0.1	0.8	27.4	8
Tob	3.6	23	3.0	4.4	11.2	1.2	3.4	18.7	31
Bra	4.5	63	1.9	1.3	10.6	1.2	1.2	25.5	11
Oxidizer treatment									
Mat	6.7	90	1.2	2.8	47.0	0.1	2.9	2.1	20
Blu	6.5	25	1.7	0.5	52.1	0.3	0.1	2.2	9
Passive treatment									
Low	6.3	72	2.0	0.2	52.6	<0.1	0.1	0.6	10
Hug	4.1	140	1.4	0.4	47.5	<0.1	<0.1	0.1	17
Hon	6.2	53	2.1	0.1	54.3	0.1	<0.1	0.4	10

The site names are shortened to provide anonymity

obviously entails many additional costs (Harrison 2013) that will substantially decrease the net profitability of the concept. However, the large difference in Fe cost and value is a primary reason the OIF concept has attracted attention.

Mine water treatment produces Fe-rich solids that could be useful in OIF projects. The opportunity for the mining industry to produce suitable Fe products will depend on the purity and mineralogy of the solids and the presence of metals that could inhibit plankton growth. Table 3 shows the elemental chemistry of solids produced by several treatment processes. The most common method for treating large loads of Fe-containing mine water is lime neutralization with aeration. These solids produced typically have a high Ca content (due to the formation of calcite), which decreases the Fe content. Alkaline Fe-contaminated mine waters treated with oxidizers produce solids with a high Fe content. Passive treatment produce solids with the highest Fe content.

The suitability of using mine drainage solids for OIF projects will depend on the bioavailability of the Fe. The solids shown in Table 3 are all produced by oxidative reactions, which form ferric iron oxide minerals. The Fe content of ferric minerals is not bioavailable. However, the Fe content of aerosol dust is also not bioavailable. The Fe in oxidized iron minerals is made bioavailable in aquatic environments by its reduction to soluble ferrous iron by photoreduction (Finden et al. 1984; McKnight et al. 1988) and by dissolved organic ligands that are commonly present in oceanic surface waters (Wells et al. 1995). The mineralogy of the iron solids affects the rate of reduction and its availability to phytoplankton (Anderson and Morel 1982; Rich and Morel 1990). It is worth noting that ferrous sulfate added by OIF experiments is only temporarily bioavailable as the half-life for ferrous iron in aerobic

oceanic surface water at pH 8 is only several minutes, while plankton blooms take days to develop. Thus, an active iron redox cycle is a necessary component of the natural or anthropomorphic stimulation of oceanic primary productivity.

A second concern about mine drainage solids is the presence of metals that could inhibit plankton growth. Copper is a potent algaecide. Perez et al. (2010) calculated an EC_{10} (concentration at which 10 % of the organisms show an adverse effect) for phytoplankton assemblages of 2.65 μg/L Cu. Table 3 includes the copper content (8–24 mg/L) for the mine water treatment solids. For the solids with a high Fe content, the Fe:Cu ratio is about 30,000:1. Applying these solids at the application rate used by Smetacek et al. (2012), would result in a total Cu concentration in the water column of approximately 10^{-6} μg/L. Based on this calculation, it does not appear that solids produced from coal mine drainage would act as algaecides, though if solids are sourced from mine water sources with much higher toxic metal concentrations, biotoxicity evaluations may be warranted. However, it appears that there is a large safety factor at the application rates presented here.

The largest potential for producing Fe products from mine drainage is found in discharges from underground mines that have large flows and Fe loading. These large discharges are typically treated with conventional lime technologies. The solids from these plants generally have a high Ca content and only contain 10–30 % Fe (Table 3). While impure, the Fe content compares favorably with $FeSO_4 \cdot 7H_2O$. If these solids can be dewatered and

processed to a dry powder, they may be substitutable for $FeSO_4 \cdot 7H_2O$.

Many large discharges from underground mines are alkaline and do not require neutralization. The use of oxidants (H_2O_2 and ozone) can be competitive with lime treatment (Means et al. 2013), especially when the mine water contains high CO_2 concentrations. Because oxidants produce solids with much higher Fe content (Table 3), there is better opportunity for making a product that might be substituted for $FeSO_4 \cdot 7H_2O$ in OIF projects. The value added by recovery of a saleable Fe by-product could substantially improve the economics of oxidant technologies.

Conclusions

The ability of Fe additions to stimulate carbon fixation in high nitrate low chlorophyll ocean waters has been established by numerous fertilization experiments. The stimulation of C-fixation produces potential value through carbon sequestration and increased fisheries. The gross value of these carbon benefits range between \$8,000 and \$11,000 per tonne of Fe. The current Fe source for OIF projects is $FeSO_4 \cdot 7H_2O$, which has a 20 % Fe content. Oxidative mine water treatment technologies can produce solids with 50–55 % Fe content, which could substitute for $FeSO_4 \cdot 7H_2O$ in fertilization projects. If the OIF concept gains widespread credibility, a new market for hundreds of thousands of tons of Fe could develop, which would provide a major opportunity for mine water treatment systems to decrease costs by producing a marketable Fe by-product.

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