Aluminum effects on marine phytoplankton: implications for a revised Iron Hypothesis (Iron-Aluminum Hypothesis)

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Abstract

In contrast to substantial studies and established knowledge of aluminum (Al) effects (mainly toxicity) on freshwater organisms and terrestrial plants, and even on human health, only a few studies of Al effects on marine organisms have been reported, and our understanding of the role of Al in marine biogeochemistry is limited. In this paper, we review the results of both field and laboratory experiments on the effects of Al on marine organisms, including Al toxicity to marine phytoplankton and the beneficial effects of Al on marine phytoplankton growth, and we discuss possible links of Al to the biological pump and the global carbon cycle. We propose a revised Iron (Fe) Hypothesis, i.e., the Fe-Al Hypothesis that introduces the idea that Al as well as Fe play an important role in the glacial-interglacial change in atmospheric CO_2 concentrations. We propose that Al could not only facilitate Fe utilization, dissolved organic phosphorus utilization and nitrogen fixation by marine phytoplankton, enhancing phytoplankton biomass and carbon fixation in the upper oceans, but also reduce the decomposition and decay of biogenic matter. As a result, Al allows potentially more carbon to be exported and sequestered in the ocean depths through the biological pump. We also propose that Al binds to superoxide to form an Al-superoxide complex, which could catalyze the reduction of Fe(III) to Fe(II) and thus facilitate Fe utilization by marine phytoplankton and other microbes. Further ocean fertilization experiments with Fe and Al are suggested, to clarify the role of Al in the stimulation of phytoplankton growth and carbon sequestration in the ocean depths.

Keywords: aluminum; marine phytoplankton; Iron Hypothesis; Fe-Al Hypothesis; beneficial effects; biological pump

1 Introduction

Aluminum (Al) is the most abundant metallic element in the Earth's crust (Taylor 1964), it is widespread in the environment, and is present in every cell of every organism (Exley and Mold 2015). Paradoxically, no established biological function of Al has yet been found.

Aluminum can be toxic to aquatic organisms and terrestrial plants, and it has even been related to some human diseases (Gensemer and Playle 1999; Macdonald and Martin 1988; Yokel 2000). In contrast to substantial studies and established knowledge of Al effects on organisms in acid and neutral pH freshwater, only a few studies of Al effects on marine organisms in seawater have been reported. Our understanding of the role of Al in marine biogeochemistry is strictly limited.

Many studies focus on the scavenging effects of marine organisms on the distribution of Al in seawater, as marine organisms, especially microbes, can adsorb Al on their surface or absorb it into cells, thus decreasing dissolved Al concentrations in seawater (e.g., Liu et al. 2017b; Moran and Moore 1988; Ren et al. 2011). In contrast, the effects of Al on marine organisms are usually unnoticed. More than five decades ago, Menzel et al. (1963) reported that Al enrichment could increase primary productivity in some waters in the Sargasso Sea. Subsequently, over the past half century, sporadic studies have reported the influences of Al on marine organisms including the early life stages of oysters, mussels, crabs, urchins and cnidarians, polychaetes, and marine algae

(Supplement material Table S1). All these studies provide a preliminary overall notion that the Al effects on marine organisms might be very different, and more diverse, compared to its mainly toxic interactions with organisms in freshwater. These results also inspired us to think that Al may play an important but unrecognized role in the global carbon cycle through influencing marine organisms, especially marine phytoplankton.

To understand the role of Al in marine biogeochemistry, we review 1) the bioavailability of Al to marine organisms, 2) Al toxicity to marine organisms, 3) beneficial effects of Al on marine phytoplankton growth, 4) the possible links of Al to the biological pump and the global carbon cycle, and 5) the relationship of Al with climate change and the Iron Hypothesis. We propose a revised Fe-Al Hypothesis to recognize the potentially important role of Al in the global carbon cycle and climate change over geological time scales.

2 Bioavailability of Al to marine organisms

2.1 Aluminum sources in natural seawater

River runoff, atmospheric dust deposition, and sediment resuspension are usually considered the main sources of Al in natural seawater (Maring and Duce 1987; Orians and Bruland 1986; van Hulten et al. 2013) (Fig. 1). Aluminum is transported with river runoff into estuaries and their adjacent coastal waters, and with the deposition of atmospheric dust into offshore seawater and the open ocean. Sediment resuspension could also release Al trapped in the bottom (biogenic and abiotic) sediments into the overlying seawater. Recent studies show that hydrothermal venting is another potentially important source of Al in the ocean (Fig. 1). Hydrothermal vents in mid-ocean ridges, such as the southern East Pacific Rise, are thought to contribute an important flux of Al into the adjacent deep ocean (Elderfield and Schultz 1996), and the Al could be transported several thousand kilometers westward across the Southern Ocean (Measures et al. 2015; Resing et al. 2015). In addition, anthropogenic activities, such as coastal mining and dredging operations, discharges of liquid wastes associated with Al production, and the use of Al in sacrificial anodes, could significantly increase local inputs of Al into natural seawater (Gillmore et al. 2016).

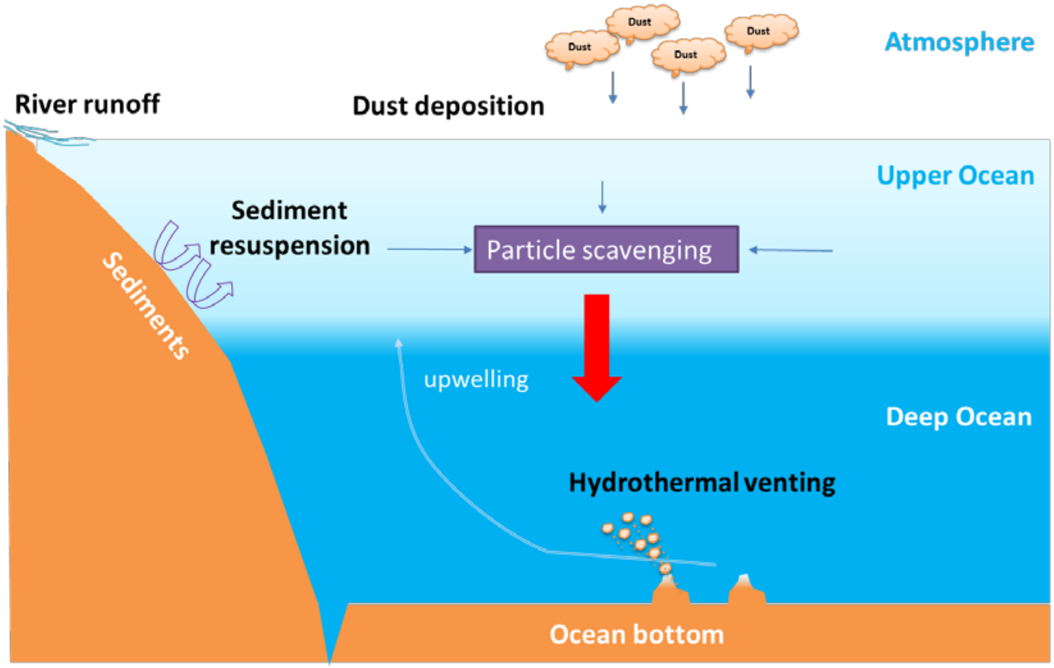

Figure 1. Schematic diagram of natural sources of Al in the ocean.

2.2 Solubility of Al in seawater

The solubility of Al is pH-dependent. Like most trivalent metals, Al is more soluble in acidic and basic solutions with a minimum in circumneutral solutions (Millero 2009). Savenko and Savenko (2011) examined the solubility of Al in artificial seawater with a salinity of 35 at 25 ^{o}C and over a pH range from 7.4 to 8.2. They found that the solubility ranged from 1.9 to 6.2 μM, with a minimum from pH 8.05 to 8.10. An Al solubility of about 10.5 μM in artificial seawater has also been reported (Machill et al. 2013).

The solubility of Al in natural seawater is significantly higher than that in artificial seawater. Willey (1975) reported that the Al solubility in filtered offshore seawater sampled in the Sargasso Sea was 18.5 μM (500 μg/L) at 2 ^{o}C and demonstrated that Al could be removed from seawater by coprecipitation with added silicic acid. He concluded that levels of dissolved Al found in seawater would vary as a function of the concentration of dissolved silica. Another two studies reported Al solubility values for filtered coastal seawater of 18.5 μM (500 μg/L) at 22 ^{o}C, and 24 μM (650 μg/L) at 28 ^{o}C, respectively (Angel et al. 2016; Trenfield et al. 2015). Owing to slow rates of precipitation and transformation of Al solid phases, dissolved Al concentrations up to 1250 μg/L (46.3 μM) could also persist for several days (Angel et al. 2016). The much higher solubility of Al in natural seawater than in artificial seawater might be partly due to the complexation of Al by strong organic ligands in natural seawater, as there is evidence indicating that siderophores, the high-affinity iron-chelating molecules secreted by microorganisms such as bacteria, could complex Al (Santos 2008).

2.3 Speciation of dissolved Al in seawater

At present, there are no analytical methods to measure the ionic and neutral dissolved forms of Al in seawater (Gillmore et al. 2016), and our knowledge about Al speciation in seawater is based almost entirely on thermodynamic calculations. Without considering the influence of organic ligands, calculations with chemical equilibrium models show that aluminate ($Al(OH)_4^-$), aluminum trihydroxide ($Al(OH)_3$) and $Al(OH)_2^+$ are the dominant Al species in alkaline seawater, although the proportions of the three species relative to total dissolved Al in seawater vary among the different models (Table 1). Based on the Miami Interactions Model (Pierrot and Millero 2017), which is designed for calculating trace metal speciation in seawater, aluminate and aluminum trihydroxide are the dominant species in the pH range (7.4 to 9.0) of natural seawater (data not shown); this result differs from the speciation proposed by Savenko and Savenko (2011), where $Al(OH)_2^+$ is the primary form of Al occurrence in seawater at $pH < 8.05$ and $Al(OH)_3$ prevails within the narrow range from pH 8.05 to 8.10. Aluminum can also react with silicic acid but this reaction tends to produce colloidal and particulate hydroxyaluminosilicates rather than dissolved species (Beardmore et al. 2016; Exley et al. 2012).

Despite the lack of agreement concerning the exact proportions of the various $Al(OH)_x^{(3-x)+}$ complexes in seawater, the species of dissolved Al in seawater are clearly very different from the main Al species in neutral and weakly acid freshwater. Generally, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and Al-fulvic are the dominant dissolved Al species in natural freshwater (Campbell et al. 1992; Driscoll and Schecher 1990).

Table 1 Speciation of dissolved Al in seawater calculated by different models at pH = 8.1 and 25 °C. Seawater composition used for the models was documented by Pierrot & Millero (2017). The total Al concentration was set as 100 nM.

Species	Miami Interactions Model	MINEQL 5.0[a] Model	Visual MINTEQ Model
$Al(OH)_2^+$	0.36%	< 0.03%	< 0.04%
$Al(OH)_3$	35.3%	0.5%	1.1%
$Al(OH)_4^-$	64.4%	99.5%	98.9%

[a] The MINEQL5.0 model predicted that ~61% of the total 100 nM Al would precipitate as diaspore; data in the table show the proportions in the remaining dissolved Al.

2.4 Dissolved Al concentrations in natural seawater

Aluminum concentrations in natural seawater vary significantly, ranging from sub-nanomolar (nM) in the open ocean (Kaupp et al. 2011; Middag et al. 2011; Planquette et al. 2009) to micromolar (µM) in estuaries. The highest Al concentrations in natural seawater occur in the estuaries, where typical Al concentrations range from 10 to several hundred nM. Concentrations as high as µM can be observed in brackish waters with low salinity in the riverine end of estuaries (Angel et al. 2016; Hall et al. 1999; Zhang et al. 1999), although, strictly speaking, the salinity at the riverine end is too low to be considered as seawater. Dissolved Al concentrations in coastal seawater and in ocean basins have been summarized by several studies (Angel et al. 2016; Han et al. 2008; van Hulten et al. 2013). These studies indicate that typical Al concentrations in coastal waters range from 10 to 100 nM, whereas typical Al concentrations in the open ocean range from sub-nM to tens of nM. The mean Al concentrations in surface seawaters in different ocean basins, such as the North Atlantic, South Atlantic, Pacific, Southern Ocean, Indian Ocean and Mediterranean Sea, were reported to range from 2.2 nM to 65.2 nM (Han et al. 2008). Clearly, Al concentrations in most of the ocean are very low, i.e., at trace levels.

2.5 Accumulation and uptake of Al by marine organisms

One of the reasons for the relatively low Al concentrations in natural seawater is that dissolved Al in seawater is usually quickly scavenged by particles, such as marine plankton (Fig. 1). Over the last several decades, a number of studies have reported that marine plankton, especially marine phytoplankton such as diatoms, could remove or scavenge dissolved Al in seawater through adsorption on their surface or/and absorption into their cells (Liu et al. 2017b; Moran and Moore 1988; Ren et al. 2011).

Consistent with the idea that Al exists in every cell of every organism (Exley and Mold 2015), marine plankton can also accumulate large amounts of Al, which is usually the most abundant trace metal in marine plankton (Collier and Edmond 1984; Ebihara et al. 2006; Kuss and Kremling 1999; Martin and Knauer 1973). In particular, marine diatoms scavenge dissolved Al in seawater efficiently, and there is evidence that marine diatoms can incorporate Al into their siliceous frustules (Gehlen et al. 2002; Koning et al. 2007; Machill et al. 2013; Moran and Moore 1988; Stoffyn 1979). Aluminum has been shown to bind to the cell walls (frustules) of marine diatoms (e.g., *Porosira glacialis*, *Thalassiosira nordenskioeldii*, *Lauderia annulata*, and *Stephanopyxis turris*), and Al/Si ratios in diatom frustules ranging from 1:10,000 to 1:15 have been reported (Beck et al. 2002; Machill et al. 2013; Van Bennekom et al. 1991). To our knowledge, there is only one published study reporting that Al could be transported into the cells of three marine diatoms (*Nitzschia closterium, Skeletonema coasatum* and *Thalassiosira weissflogii*). However, in this laboratory study (Wang et al. 2013), truly intracellular Al was not distinguished from the fraction of Al that was strongly bound to the cell surface (i.e., the siliceous cell wall) and could not be removed by washing solutions designed to remove metals weakly adsorbed onto the cell surface. Our own unpublished data indicate that the Al internalization flux for a model marine diatom (*Thalassiosira weissflogii*), normalized to the exposure concentration, was 0.033 ± 0.013 nmol/m^2/min/nM, and the assimilated Al was distributed in descending order of importance among the following subcellular fractions: granules (68.7 ± 5.4%), debris (17.3 ± 3.6%), organelles (11.9 ± 2.1%), heat-stable peptides (1.8 ± 0.2%), and heat-denaturable proteins (0.4 ± 0.0%).

Exley and Mold (2015) identified five major routes by which Al could traverse cell membranes or epi-/endo-thelia, including paracellular transport, transcellular transport, active transport, ion channels and adsorptive or receptor-mediated endocytosis. They suggested that Al could be assimilated in this manner in a number of forms: 1) free solvated trivalent cation, 2) low molecular weight, neutral, soluble complexes, 3) high molecular weight, neutral, soluble complexes, 4) low molecular weight, charged, soluble complexes, and 5) nano and micro-particulates. However, for trivalent metals such as Al, these uptake mechanisms are still speculative, as a result of insufficient study and technical challenges. The aqueous coordination chemistry of Al is complex (e.g., slow kinetics and metastable poly-Al forms), it binds strongly to biological surfaces, no affordable and suitable radioisotopes are available and sensitive analytical techniques seldom exist (Crémazy et al. 2013; Rengel 1996; Taylor et al. 2000). To our knowledge, there are no studies on the uptake kinetics of Al assimilation by marine organisms, let alone on the mechanisms of Al transport into marine phytoplankton cells. Overall, we know very little about the bioavailability of Al to marine organisms.

3 Al toxicity to marine organisms

There are very few studies reporting the effects (including toxicity) of Al on marine organisms. To the best of our knowledge, only 29 published studies (excluding studies of the influence of Al on diatom frustules) report on the effects of Al on marine organisms (supplemental material Table S1); more than half of the studies (16) have been published since 2010, and only 16 of the studies were intentionally designed to test the acute toxicity of Al to marine organisms or organisms in brackish waters.

Tolerance of high concentrations of Al by marine animals has been highlighted by a number of studies. The toxicity of Al to the early life stages (embryonic development, fertilization rates, etc.) of marine invertebrates such as oysters, mussels, crabs, urchins, cnidarians and polychaetes has been relatively substantially covered in early (Calabrese et al. 1973; Macdonald et al. 1988; Pagano et al. 1996; Petrich and Reish 1979; Wilson and Hyne 1997) and recent studies (Caplat et al. 2010; Golding et al. 2015; Negri et al. 2011). The Al toxicity to copepods and fish in brackish water, and to fish in seawater, has also been documented (Bengtsson 1978; Golding et al. 2015; Teien et al. 2006). These studies demonstrate that Al toxicity only occurs at µM concentrations or above for most of the tested animal species (supplemental material Table S1).

Aluminum toxicity to marine phytoplankton has only been intentionally tested in recent years (Gillmore et al. 2016; Golding et al. 2015; Harford et al. 2011; Saçan et al. 2007; Xie et al. 2015). The influence of Al on the growth, iron (Fe) uptake and physiology of marine phytoplankton has also been reported in other studies (Liu et al. 2018; Santana-Casiano et al. 1997; Shi et al. 2015; Stoffyn 1979; Vrieling et al. 1999; Zhou et al. 2016). Among all the 13 marine phytoplankton species tested (Table S1), the growth of only one diatom *Ceratoneis closterium* was reported to be inhibited by environmentally relevant Al concentrations (higher than about 10 µg/L or 0.37 µM) in one study (Golding et al. 2015), but its growth was reported to be stimulated by low Al concentrations (< 60 µg/L or < 2.2 µM) in another study (Gillmore et al. 2016). Similarly, the growth and nitrogen fixation of the cyanobacterium *Crocosphaera watsonii* were inhibited by a low Al concentration (200 nM) in a phosphorus-sufficient seawater medium (Liu et al. 2017a), but they were stimulated by the same Al concentration in the same seawater medium but with insufficient phosphorus (Liu et al. 2018). Overall, based on the existing published data, environmentally relevant Al concentrations will not be toxic to most marine phytoplankton species in natural seawater.

It should be pointed out here that recent studies show that the Al effects on marine phytoplankton are closely related to the nutrient status of the algal growth medium (Liu et al. 2017a; 2018; Zhou et al. 2016). In future studies, nutrient conditions in the medium used for Al toxicity tests should be considered as a potential factor influencing the toxicity test results. We speculate that different background nutrient concentrations in the seawater used for preparing the test media might account for the inconsistent toxicity results for *Ceratoneis closterium* (Golding et al. 2015; Gillmore et al. 2016).

Consistent with the above discussion and based on toxicity tests of 11 species from 6 taxonomic groups, Golding et al. (2015) estimated that 2.1 μg/L and 24 μg/L of Al (i.e., 78 and 890 nM) would be safe for 99% and 95% of marine species, respectively. Although our understanding of Al effects on marine organisms is far from sufficient, based on our present knowledge about Al concentrations in natural seawater (discussed in Section 2.4), we would expect that natural levels of Al in most of the ocean will show no toxicity to marine organisms living there.

4 Beneficial effects of Al on marine phytoplankton growth

4.1 Enhanced growth of marine phytoplankton in the presence of Al

In contrast to Al toxicity, there are several studies reporting that Al could be beneficial to the growth of marine phytoplankton, "growth" being defined in the present context as the exponential growth rate and/or biomass yield.

Since Menzel et al. (1963) first reported that Al enrichment increased the primary productivity in some waters in the Sargasso Sea, additional evidence indicating the beneficial effects of Al on marine phytoplankton growth has been sporadically published. Stoffyn (1979) reported the stimulatory effects of Al on the growth of a marine diatom

Skeletonema costatum during a study on diatom control of dissolved Al in seawater. Twenty years later, it was reported that enrichments with Al (0.1 to 10 µM) increased growth of a pennate diatom *Navicula salinarum* (Vrieling et al. 1999). Enhanced growth of other marine phytoplankton species (*Dunaliella tertiolecta*, *Tetraselmis* sp., and *Ceratoneis closterium*) in the presence of Al was unexpectedly observed during tests of Al toxicity to marine phytoplankton (Gillmore et al. 2016; Golding et al. 2015; Saçan et al. 2007). Similar stimulatory effects of Al enrichment on marine phytoplankton growth (e.g., *Synechococcus* sp., *Thalassiosira weissflogii* and *Crocosphaera watsonii*) were reported in laboratory studies (Leleyter et al. 2016; Liu et al. 2018; Shi et al. 2015; Shi et al. 2016; Zhou et al. 2016). Enhanced growth of marine phytoplankton (e.g., Diatoms, *Trichodesmium*, photosynthetic picoeukaryotes, unicellular diazotrophic cyanobacterium group A, *Synechococcus* and *Prochlorococcus*) in the presence of added Al has also been observed in field studies (Liu et al. 2018; Shi et al. 2016; Zhou et al. 2017). Our unpublished data indicate that Al enrichment (40 nM and 200 nM) enhanced the yield of all the tested diatoms, namely *Thalassiosira oceanica*, *T. pseudonana*, *Phaeodactylum tricornutum* and *Chaetoceros muelleri*, in phosphorus-deficient Aquil medium (Zhou et al. unpublished manuscript).

4.2 Enhanced nitrogen fixation in the presence of Al

Previous studies indicate that Al is linked to nitrogen fixation and nitrogen-fixers. Positive correlations between dissolved Al, nitrogen fixation and *Trichodesmium* abundance have been reported in the Atlantic Ocean (Moore et al. 2009; Rijkenberg et al. 2011). In these studies Al was treated only as an indicator of terrigenous dust (/Fe) input, and the roles of Al in influencing nitrogen fixation and nitrogen-fixers were usually unnoticed. In fact, *Trichodesmium* could not only accumulate a large amount of Al (e.g., 2.6 μmol/μg chlorophyll-*a*) (Moore et al. 2009; Tovar-Sanchez et al. 2006), but it also contains a gene of unknown function involved in Al resistance (da Cunha et al. 2009).

A recent study shows that enhanced nitrogen fixation and increased growth of nitrogen-fixers occurs in the presence of Al. By adding Al to natural seawater collected from the South China Sea, a large subtropical and tropical marginal sea, we observed enhanced growth of *Trichodesmium*, and increased nitrogen fixation by the whole plankton community (Zhou et al. 2017). Another study indicated that addition of a low level of Al (200 nM) to natural seawater in the South China Sea could not only stimulate nitrogen fixation by the whole plankton community, but could also increase the growth and the *nifH* gene expression of two nitrogen-fixers (*Trichodesmium* spp. and unicellular diazotrophic cyanobacterium group A (Liu et al. 2018). Stimulatory effects of Al on the growth and nitrogen fixation of the unicellular diazotrophic cyanobacterium *Crocosphaera watsonii* in phosphorus-deficient Aquil medium have also been confirmed in a laboratory study (Liu et al. 2018).

4.3 Enhanced uptake of Fe in the presence of Al

Another beneficial effect of Al on marine phytoplankton growth is that some marine diatoms increase their Fe uptake in the presence of Al. Santana-Casiano et al. (1997) reported that the Fe uptake by *Thalassiosira weissflogii* increased in the presence of Al. They suggested that an increase of labile Fe could be one of the reasons for increased Fe uptake by the diatom in the presence of Al. However, they recognized that the mechanism for the transformation reactions from stable Fe-organic complexes, inorganic crystalline Fe hydrolysis products and small Fe colloids to labile Fe was not clear.

New understanding of Fe uptake by marine microorganisms, and the catalytic role of Al in the reduction of Fe(III) to Fe(II), suggests a new perspective on why the presence of Al could increase Fe uptake by marine phytoplankton. On the one hand, extracellular reduction of Fe (III) to Fe (II) is considered a prerequisite for Fe uptake by most phytoplankton (Shaked et al. 2005), and an Fe-acquisition strategy allowing other microbes (such as denitrifiers or anammox-capable species) to succeed in regions where the concentrations of bioavailable Fe are exceedingly low (Kondo and Moffett 2015; Moffett et al. 2007). Extracellular reduction of Fe(III) complexes by biogenic superoxide is an important way of producing Fe(II) (Rose and Waite 2005). Besides photochemical production of superoxide in the marine environment, many marine organisms including diatoms, cyanobacteria and heterotrophic bacteria can produce superoxide, which is capable of reducing a wide range of forms of Fe(III) under typical environmental conditions, such as those found in many marine systems (Diaz et al. 2013; Hansel et al. 2016; Rose 2012; Schneider et al. 2016).

On the other hand, Al can potentially facilitate the reduction of Fe(III) to Fe(II) and increase Fe availability to marine organisms. First, Al has an intrinsic high potential to stabilize the superoxide anion (Exley 2004; Mujika et al. 2011). This could increase the lifetimes of superoxide long enough to enable it diffuse well away from the site of its production, and influence the reduction of Fe(III) on a spatial scale that is biologically significant (Rose 2012). Second, Al could bind with superoxide to form an Al-superoxide complex, catalyzing the reduction of Fe(III) to Fe(II), and increasing the concentration of Fe(II) (Exley 2004; Khan et al. 2006; Mujika et al. 2011; Ruipérez et al. 2012); the result would be an increase in labile and readily internalized Fe (Fig. 2).

Accordingly, we hypothesize that Al can facilitate Fe uptake by marine phytoplankton and other microbes through forming an Al-superoxide complex, catalyzing the reduction of Fe(III) to Fe(II) and increasing Fe bioavailability. The superoxide could be biogenic in origin or from other external sources, as discussed above.

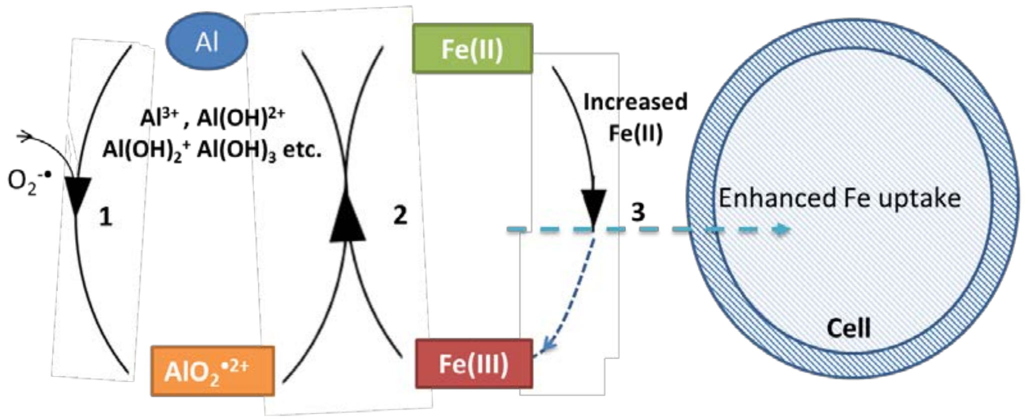

Figure 2 Schematic diagram illustrating how Al could facilitate Fe uptake by marine phytoplankton and other microbes. 1. Al binds with superoxide to form an Al-superoxide complex (e.g. $AlO_2^{\bullet 2+}$); 2. Al-superoxide catalyzes the reduction of Fe (III) to Fe (II); 3. Increased bioavailability of Fe (II) results in enhanced Fe uptake by phytoplankton (or other microbial) cells. The thermodynamic tendency to form Al-superoxide is Al species-dependent, and it decreases in the following order: Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ (Ruipérez et al. 2012).

4.4 Aluminum facilitates dissolved organic phosphorus (DOP) utilization by marine phytoplankton

Zhou et al. (2016) suggested that the Al-related enhanced utilization of DOP could account for the increased yield of marine phytoplankton that was observed in the presence of Al under conditions of phosphorus limitation. To examine why Al enrichment could stimulate the yield of *Thalassiosira weissflogii* in phosphorus-deficient media, but did not influence diatom growth and yield in phosphorus-sufficient media, they demonstrated that the Al-treated *T. weissflogii* cells utilized DOP at a higher rate than the control cells under conditions of phosphorus limitation. Their results indicate that Al enrichment led to a higher proportion of alkaline phosphatase activity (APA) being associated with the diatom cell surface, and a lower proportion of APA in dissolved form. More interestingly, the Al-treated diatom cells could use cellular APA more efficiently to utilize DOP than could the control cells, as the ratio of DOP uptake rate to cellular APA was significantly higher for the Al-treated cells than for the control cells. The increased yield of other diatom species (*Thalassiosira oceanica*, *Thalassiosira pseudonana*, *Phaeodactylum tricornutum*, *Chaetoceros muelleri*) and growth of one nitrogen-fixing cyanobacterium (*Crocosphaera watsonii*) in the presence of Al in phosphorus-deficient Aquil media could also be related to the enhanced utilization of DOP (Zhou et al. unpublished manuscript and Liu et al. 2018).

It should be pointed out that, despite the demonstration of enhanced utilization of Fe and DOP by marine phytoplankton in the presence of Al, we are still far from a full understanding of the mechanisms underlying the beneficial effects of Al on marine phytoplankton. Beneficial effects of Al on terrestrial plants (such as tea trees) have been reported, and several mechanisms including increasing Fe availability, promotion of nitrogen, phosphorus and potassium uptake, protection against copper, manganese and phosphorus toxicity, and alleviation of H^+ toxicity have been proposed for different plant genotypes and growth media (reviews in Foy (1984); Osaki et al. (1997)). As no established biological function of Al has yet been found, the suggestion of indirect roles of Al in the enhanced growth of marine phytoplankton is more readily accepted by most of us who are accustomed to thinking of Al as a non-essential element that is toxic to freshwater organisms and terrestrial plants and animals. However, we suggest that our thinking and exploration of the roles of Al in the enhanced growth of marine phytoplankton should not be constrained by established mechanisms of action, since our understanding of Al effects on marine organisms is still embryonic and limited.

5 Possible links of Al to the biological pump and global carbon cycle

More and more evidence shows that Al could play an important role in the biological pump and the global carbon cycle, by influencing marine phytoplankton growth and biogenic matter decay. First, the beneficial effects of Al on marine phytoplankton growth, as described in section 4, indicate that Al could increase carbon fixation in the upper layers of the ocean. On the one hand, by facilitating the uptake of Fe by marine phytoplankton, Al could enhance carbon fixation in the high-nutrient-low-chlorophyll (HNLC) oceans such as the Southern Ocean, and nitrogen fixation and carbon fixation in the oligotrophic tropical and subtropical oceans. On the other hand, by enhancing phytoplankton utilization of DOP, Al could increase carbon fixation in coastal seawaters such as estuaries, where phosphorus limitation can sporadically occur (Lin et al. 2016), and in phosphorus-limited oligotrophic seawater such as the tropical Atlantic Ocean

(Browning et al. 2017). The Al-related enhanced carbon fixation in the upper oceans would provide increased organic carbon could potentially be exported to the deep ocean through the biological pump.

Second, Al could increase the proportion of organic carbon fixed in the upper ocean that is exported and sequestered in the deep ocean, by reducing the decomposition and decay of particulate biogenic matter. It is well known that Al can reduce the solubility of diatom frustules when it is incorporated into them (Beck et al. 2002; Dixit et al. 2001; Sarmiento and Gruber 2006; Van Cappellen et al. 2002), potentially leading to an increased flux of diatom frustules and associated organic matter into the deep ocean. In addition, Al has been reported to be the most abundant trace metal in fecal pellets produced by zooplankton (e.g., salps) (Cabanes et al. 2017); we suggest that the presence of Al could reduce the solubility and degradation of these pellets, which show higher export efficiencies to the deep ocean than the bulk of sinking particulate organic carbon (Anderson 1998; Cabanes et al. 2017). According to our recent unpublished laboratory data on the microbial degradation of senescent marine diatom cells, the decay of particulate organic carbon fixed by the diatoms was delayed in the presence of Al, and this was accompanied by an increase in cell size and cellular carbon content. All of these effects of Al on particulate biogenic matter would tend to increase the efficiency of the biological pump, leading to increased export of particulate organic carbon produced in the upper ocean to the deep ocean.

Third, Al can substitute for other cations (e.g., Mg) in biological systems, reacting with biomolecules to form strong bonds that are slow to dissociate (Exley and Mold 2015; Williams 1996). In addition, Al can induce the formation of strong structures in a wide range of peptides, through binding amino acid sidechains (Mujika et al. 2017). Binding to the peptide backbone has also been considered (Mujika et al. 2014; Song et al. 2014) but is less favored (Mujika et al. 2017). As a result, Al may make organic carbon more difficult to decompose, again leading to greater and longer sequestration in the ocean depths.

In summary, we suggest that Al likely plays an unrecognized but important role in the marine and global carbon cycles, not only by enhancing CO_2 fixation in the upper ocean, but also by favouring the export and sequestration of the fixed carbon to the deep ocean.

6 The relationship of Al with climate change and Iron Hypothesis

The possible links of Al to the biological pump and the global carbon cycle, and the inverse correlation of Al inputs into the Southern Ocean with atmospheric CO_2 in geological times, indicate that Al may play an important role in climate change.

6.1 A flaw in the Iron Hypothesis

The Iron Hypothesis was proposed by John Martin, who considered that higher Fe (dust) input into the Southern Ocean was associated with cooler temperatures and lower atmospheric CO_2 concentrations in geological times. This hypothesis was based on the data recorded in the Vostok ice core, which indicated that Fe inputs into the Southern Ocean were inversely correlated with atmospheric CO_2 concentrations over the past 160 thousand years (Martin 1990). The hypothesis led to the idea that adding Fe to the ocean surface waters in the Fe-limited HNLC oceans such as the Southern Ocean would stimulate the growth of marine phytoplankton such as diatoms, drawing down atmospheric CO_2 and in turn cooling the planet. More and more paleo-oceanographic data (Abelmann et al. 2006; Kumar et al. 1995; Lambert et al. 2008; Martínez-García et al. 2014; Martínez-Garcia et al. 2011), as well as modern evidence from natural Fe fertilization through dust deposition or upwelling in the Fe-limited HNLC oceans (Bishop et al. 2002; Blain et al. 2007; Han et al. 2006; Pollard et al. 2009), support the proposed link of Fe to climate change, i.e., inputs of Fe into the HNLC oceans would result in phytoplankton blooms in the upper layer, and carbon export and sequestration in the deep ocean.

However, the Iron Hypothesis is only partly supported by experimental ocean Fe fertilizations conducted in Fe-limited seawaters all over the world. To examine the idea that Fe fertilization might control past and future climate, as predicted by the Iron Hypothesis, 13 ocean Fe fertilization experiments in Fe-limited seawaters, such as the Southern Ocean, have been completed since 1993. Adding Fe indeed brought about phytoplankton blooms in the upper ocean, but it did not necessarily result in increased carbon export and sequestration into the deep ocean (Boyd et al. 2007; Boyd et al. 2004; Martin et al. 2013). In contrast, enhanced carbon export to the deep ocean was consistently observed following natural Fe fertilization; natural Fe fertilization was 10 to 100 times more efficient at removing carbon from the surface ocean than any artificial Fe fertilization has been (Blain et al. 2007; Pollard et al. 2009; Salter et al. 2014; Wolff et al. 2011). This observation led us to consider that Fe alone could not adequately explain the drawdown of atmospheric CO_2 concentrations and cooler temperatures in glacial periods, i.e., there could be a flaw in the Iron Hypothesis, and the differences between natural and experimental Fe fertilizations may tell us where the flaw lies.

6.2 A revised Iron-Aluminum Hypothesis

Natural Fe fertilization, as caused by dust deposition, upwelling and hydrothermal venting, provides the ocean not only Fe, but also Al and other elements. Silicate and phosphorus from dust deposition have been suggested to favor net primary production and a greater carbon sink in the ocean (Falkowski et al. 1998; Harrison 2000). It is also well established that dust deposition is the major source of dissolved Al in the upper layer of the open ocean, most of this Al being in the form of aluminosilicates. Several studies have reported the solubility of Al in dust aerosols (e.g., Baker et al. 2006; Buck et al. 2013; Measures et al. 2010). The median solubility is around 5%, and 80% of the dissolvable Al in dust aerosols is released rapidly in seawater, within the first 24 h, and a further 20% is released slowly over the next three days (Measures et al. 2010).We here propose that the Al associated with natural Fe fertilization may be responsible for the inconsistency between natural and experimental Fe fertilization events.

- Re-examining the argument for the Iron Hypothesis, we find that the original data from the Vostok ice core showed an inverse correlation not between Fe and CO_2, but rather between Al and CO_2 (Fig. 3). Martin converted the original Al data to Fe estimates using Taylor's (1964) crustal abundance values (Martin 1990). In other words, the original data also support the idea that higher Al inputs into the Southern Ocean were associated with cooler temperatures and lower atmospheric CO_2 concentrations in geological times (De Angelis et al. 1987; Petit et al. 1999).

- As discussed earlier, with reference to the effect of Al on various biogeochemical processes (Section 4), this Al could allow marine phytoplankton to use the Fe inputs from natural processes like dust deposition or hydrothermal venting more efficiently.
- Finally, the ability of Al to reduce the decomposition and decay of biogenic matter could favor the export of the Fe fertilization-generated organic carbon in HNLC oceans to the deep ocean. Moreover, Al could also potentially increase carbon export and sequestration in non-HNLC oceans by stimulating nitrogen fixation and facilitating the utilization of Fe and DOP by marine phytoplankton, as discussed in Section 4.

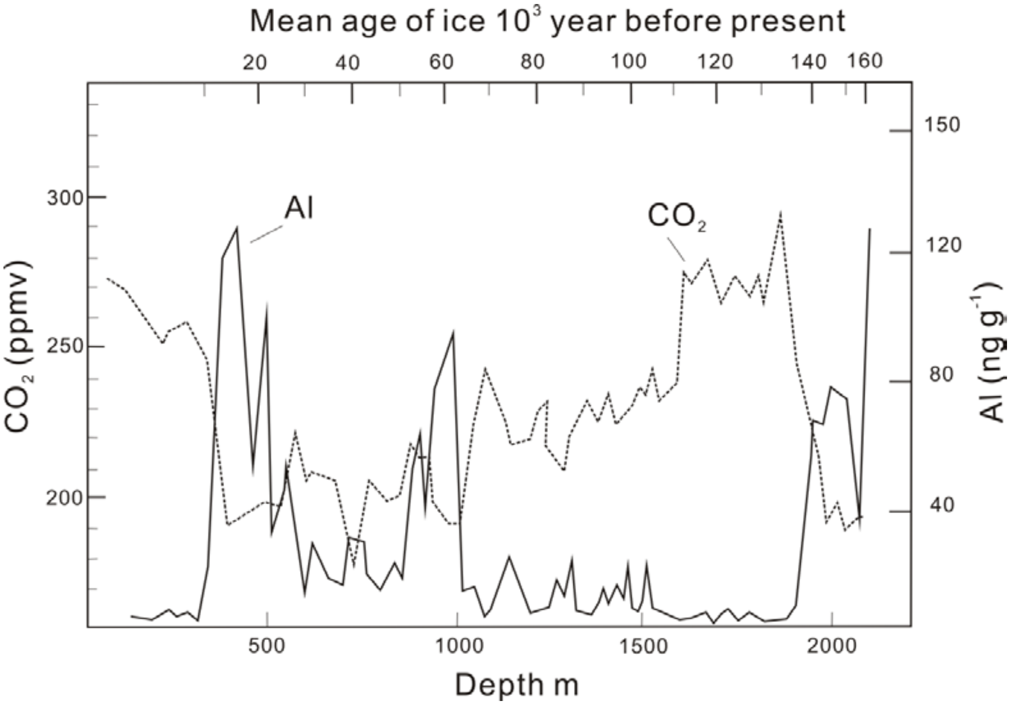

Figure 3. Al concentrations as a function of real depth in the Antarctic Vostok ice core, together with mean CO_2 concentrations in air trapped in ice, versus mean age

of ice. Original figure adapted from Martin (1990). Al data are from De Angelis et al. (1987); CO_2 concentrations are from Barnola et al. (1987).

Accordingly, we would like to propose a revision to the original Iron Hypothesis, to propose a new Fe-Al hypothesis that takes into account the roles played by Al as well as Fe in the glacial-interglacial change in atmospheric CO_2 concentrations and climate change. In the new hypothesis, we do not deny the important role of Fe, but seek recognition that the role of Al is also important in the global carbon cycle, as outlined in Fig. 4. We predict that adding both Al and Fe in the HNLC oceans such as the Southern Ocean, will result not only in phytoplankton blooms in the upper ocean, but also high carbon export and sequestration to the deep ocean.

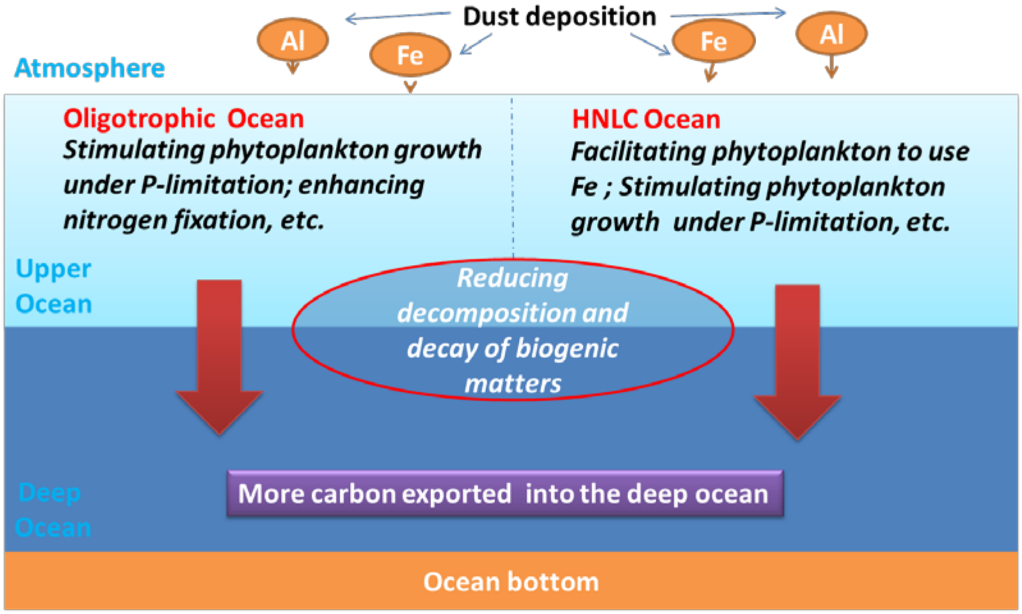

Figure 4. Schematic description of the revised Fe-Al Hypothesis. Natural Fe fertilization processes like (but not limited to) dust deposition provide the ocean not only with Fe but also Al; Al, as well as Fe, plays an important role in the glacial-interglacial change in atmospheric CO_2 concentration and climate change.

Acknowledgements

We thank Dr. Fengjie Liu for helpful discussion of our work. This work is supported by the National Key Basic Research Program of China (973 Program, 2015CB452904), the National Natural Science Foundation of China (41506150), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA11020305), and the Science and Technology Planning Project of Guangdong Province, China (2017B030314052), the Natural Science Foundation of Guangdong Province, China (2015A030310169) and the Natural Sciences and Engineering Research Council of Canada (NSERC). C. Fortin and P.G.C. Campbell benefitted from support from the Canada Research Chairs program.

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