Aluminum increases net carbon fixation by marine diatoms and decreases their decomposition: Evidence for the iron–aluminum hypothesis

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Abstract

Recent studies indicate that aluminum (Al) could play an important role in the ocean carbon cycle by increasing phytoplankton carbon fixation and reducing organic carbon decomposition. However, how Al may influence the decomposition of organic carbon has not yet been explicitly examined. Here we report the effects of Al on carbon fixation by marine diatoms and their subsequent decomposition. By using radiocarbon as a tracer, the carbon fixation and decomposition of three model marine diatoms were examined in Aquil® media at different concentrations (0, 40, 200, and 2000 nM) of dissolved Al. Addition of Al enhanced net carbon fixation by the diatoms in the declining growth phase (by 9%–29% for Thalassiosira pseudonana, 15%–20% for T. oceanica, 15%–23% for T. weissflogii). Under axenic conditions the decomposition rates (d⁻¹) of the diatom-produced particulate organic carbon (POC) significantly decreased (by 21%–57% for T. pseudonana, 0%–41% for T. oceanica, 29%–58% for T. weissflogii) in the Al-enriched treatments. In the presence of bacteria, the decomposition rates of T. weissflogii-produced POC were still 37%–38% lower in Al-enriched treatments compared to the control. Significant increases in cell size, cellular carbon content (pmol C/cell) and cellular carbon density (pmol C/μm³) of T. weissflogii were also observed in the Al-enriched treatments compared to the control. The Al-related increase in net carbon fixation and cell size, and the decrease in POC decomposition rate may facilitate carbon export to ocean depths. The study provides new evidence for the iron–aluminum hypothesis, which suggests that Al could increase phytoplankton uptake of atmospheric CO₂ and influence climate change.

Aluminum is the most abundant metal element in the Earth’s crust, and its molar concentrations in the upper ocean are usually one order of magnitude higher than those of other trace metals such as iron (Bowie et al. 2002; Grand et al. 2015a; b). However, little attention is given to the effects of Al on marine organisms (Golding et al. 2015; Gillmore et al. 2016; Zhou et al. 2018). A growing body of work indicates that Al can be beneficial to the growth of marine phytoplankton (Zhou et al. 2016; Liu et al. 2018; Zhou et al. 2018a), a major driver of global CO₂ cycling (Falkowski 2012). The beneficial effects of Al on the growth of marine phytoplankton were sporadically reported in early studies (Menzel et al. 1963; Stoffyn 1979; Vrieling et al. 1999). Recent laboratory and field studies have increasingly documented that Al markedly enhanced the growth of marine phytoplankton including diatoms, cyanobacteria, and dinoflagellates (Golding et al. 2015; Leleyter et al. 2016; Zhou et al. 2018a). We have previously found that increased use of dissolved organic phosphorus (DOP) is one of the mechanisms underlying the beneficial effects of Al on marine diatoms and nitrogen-fixing cyanobacteria in phosphorus-deficient conditions (Zhou et al. 2016; Liu et al. 2018). Marine phytoplankton and other microbes can produce extracellular alkaline...
phosphatase to use DOP in phosphorus-deficient conditions (Perry 1972; Davis and Mahaffey 2017). Aluminum addition leads to a higher proportion of alkaline phosphatase associated with cell surface rather than being released into seawater. The alkaline phosphatase associated with Al-treated cells compared to the control has a higher efficiency (i.e., for each unit of alkaline phosphatase activity, there is greater uptake of DOP) and facilitates the cells’ use of DOP (Fig. 1; Zhou et al. 2016). Moreover, we hypothesize that Al can increase the uptake of iron by marine phytoplankton through coupling with superoxide to catalyze the transformation of ferric iron (Fe(III)) to ferrous iron (Fe(II)) in seawater (Zhou et al. 2018a). Extracellular reduction of Fe(III) to Fe(II) is often a prerequisite for iron uptake by marine phytoplankton, but Fe(II) is easily oxidized to Fe(III) in oxygenated seawater (Shaked et al. 2005). Superoxide in marine waters is capable of reducing a wide range of forms (e.g., inorganic, organically complexed and even solid forms) of Fe(III) to Fe(II) (Rose 2012). Aluminum exhibits a significant pro-oxidant activity (Exley 2004; Mujika et al. 2011). Theoretical calculations indicate that Al can bind with superoxide to form an Al-superoxide complex, which catalyzes the reduction of Fe(III) to Fe(II) (Ruipérez et al. 2012), and would favor Fe uptake by marine phytoplankton (Fig. 1). However, more work is needed to examine the pH-dependence of this interaction, given the influence of pH on Al speciation in seawater.

In addition to the Al-enhanced growth of marine phytoplankton, the metal may also reduce the decomposition of biogenic organic carbon in the ocean (Zhou et al. 2018b). For example, carbon degradation is likely slow in the Al-enriched frustules, since marine diatoms can incorporate Al into their siliceous frustules (Gehlen et al. 2002; Koning et al. 2007; Machill et al. 2013), and Al can reduce the dissolution rate of diatom frustules (Dixit et al. 2001; Beck et al. 2002; Van Cappellen et al. 2002). On the other hand, once it has been internalized (Liu et al. 2019), Al will bind with biomolecules (Exley and Mold 2015). The Al-binding biomolecules would be difficult to dissociate and decompose, because Al can form strong bonds and structures with a diversity of biomolecules (Song et al. 2014; Exley and Mold 2015; Mujika et al. 2018). In a summary of these various factors, our recent review paper suggested that Al may play an important role in the ocean carbon cycle and climate change, by enhancing carbon fixation in the upper ocean and by facilitating carbon export and sequestration in ocean depths by reducing the decomposition and decay of organic matter (Zhou et al. 2018b). However, this latter suggestion (i.e., how Al influences the decomposition of organic matter) has not yet been explicitly examined.

We hypothesized that Al at environmentally relevant levels could not only increase carbon fixation by marine phytoplankton but also significantly decrease the decomposition rate of the phytoplankton-produced organic carbon. To examine this hypothesis, radiocarbon (14C) was used as a tracer to examine the effects of Al on carbon fixation by three model marine diatoms and on the decomposition of the diatom-produced organic carbon. The present results are consistent with the hypothesis.

### Materials and methods

#### Cultures of marine diatoms

Cultures of the marine diatoms *Thalassiosira weissflogii* (CCMP1336), *T. pseudonana* (CCMP1335), and *T. oceanica* (CCMP1006) were obtained from the National Center for Marine Algae and Microbiota—Bigelow Laboratory for Ocean Sciences (USA). Axenic algal cultures were maintained in standard Aquil* medium (Sunda et al. 2005) contained in polycarbonate bottles at 20°C under constant illumination (100 μmol/m²/s).

#### Preparation of reagents and solutions

For culturing the diatoms, standard Aquil* medium with 100 μM nitrate, 10 μM phosphate, 10 μM silicate, vitamins (5.5 × 10⁻⁷ g/L vitamin B₁₂, 5.0 × 10⁻⁷ g/L biotin and 1.0 × 10⁻⁴ g/L thiamine), and trace metals (1.0 μM iron, 79.7 nM zinc, 121 nM manganese, 50.3 nM cobalt, 19.6 nM copper, 100 nM molybdenum and 10 nM selenium) buffered with 100 μM ethylenediaminetetraacetic acid (EDTA) was prepared with trace-metal clean artificial seawater (Sunda et al. 2005), which had an initial residual Al concentration of 24.7 ± 4.0 nM.

Low-phosphorus Aquil* medium with only 100 nM phosphate (and the other nutrients at the same concentrations as in the standard Aquil* medium) was prepared for the experimental cultures to limit the marine diatom biomass yield and avoid changes in the culture media pH. Aluminum concentrations of 40, 200, and 2000 nM were set by adding the appropriate volumes of 40, 200, and 2000 μM AlCl₃ (trace metal grade 99.9995%, Puratonic) stock solutions prepared in 0.01 M HCl (Optimum grade, Fisher Scientific) to the experimental medium, respectively, and hence the same amount of the carrier HCl solution was added into each treatment. These Al concentrations resemble those in open oceans.
receiving high dust deposition (40 nM) (Menzel Barraqueta et al. 2019), the upper limit of dissolved Al in natural seawater (200 nM), and the concentration in estuarine waters (2000 nM), respectively (Zhou et al. 2016). All the added Al will remain in the dissolved form in the culture media (Liu et al. 2019), and the vast majority (99.9%) of the aqueous Al is present in the form of aluminate (Al(OH)4−), aluminum trihydroxide (Al(OH)3), and aluminum dihydroxide (Al(OH)2+) (Zhou et al. 2018b). Aluminum will not form complexes significantly with EDTA or phosphate in alkaline seawater (Zhou et al. 2016; Liu et al. 2019).

Trace-metal-grade sodium nitratate (99.999%, Puratronic™) and sodium dihydrogen phosphate monohydrate (99.998%, Puratronic™) were used to prepare the stock solutions and the media. Artificial seawater and the polycarbonate bottles were sterilized by microwaving, and macronutrients, micronutrients, and vitamins were sterilized by 0.2μm-syringe filtration (Sunda et al. 2005). All the bottles and tubes used for preparing the reagents and solutions were trace-metal clean. All the media and solutions were prepared and allowed to sit overnight to reach chemical equilibrium before being used in a sterile, particle-free laminar flow hood.

**Experimental designs**

**Axenic cultures**

Axenic marine diatom cells in standard Aquil™ medium were transferred to the axenic low-phosphorus Aquil™ medium to acclimate for at least 10 generations. After the acclimation, the diatom cells (100μL aliquots) in exponential growth phase were transferred to the axenic experimental media to reach an initial cell abundance of 60 cells/mL for *T. weissflogii*, 80 cells/mL for *T. oceanica*, and 240 cells/mL for *T. pseudonana*. Three Al concentrations (0, 40, and 200 nM) were set for the cultures of all the three diatoms, except that an additional higher Al concentration of 2000 nM was also tested for the culture of *T. weissflogii*. Three or two replicates were run for each treatment, given the good reproducibility among the biological replicates.

Radioactive NaH14CO3 (10 μCi/mL) in small ampoules was added to the media to attain a radioactivity of 1.48 × 104 or 2.96 × 104 Bq/mL (0.62 or 1.24 × 108 Bq/mol C) to monitor the accumulation and decomposition of organic carbon in the media (Steemann Nielsen 1952). Particulate organic 14C (PO14C) was collected by filtering 3–10 mL of the cultures through polycarbonate membranes with a pore size of 0.2μm (Isopore™ membrane filters, Merck Millipore). After the filtration, diatom cells together with the filter were transferred to a scintillation vial. Dilute hydrochloric acid (1 mL, 1% HCl) was added to the vial to remove dissolved inorganic carbon in the sample for 20 min, and then 10 mL of the scintillation cocktail (Ecolume™, MP Biomedicals) were added to the vials and mixed thoroughly by vortexing. For measuring dissolved organic 14C (DO14C) in the cultures, 30 μL of 4 M HCl was added to 1 mL of the 0.2-μm filtered filtrate in a scintillation vial, mixed and set aside for 20 min to remove any inorganic carbon before addition of 10 mL of the scintillation cocktail. The 14C radioactivity was measured with a liquid scintillation analyzer (Tri-Carb 2910 TR, Perkin Elmer). Values for POC and dissolved organic carbon (DOC) were calculated based on 14C radioactivity, and the known specific activity of the carbon.

Parallel clean cultures of *T. weissflogii* were prepared without adding 14C, to monitor the cell abundance, total cell volume and cell size distribution with an electronic particle counter (Multisizer 3 Coulter Counter with a 70-μm aperture; Beckman). All the experimental cultures in polycarbonate bottles were kept at 20°C under constant illumination (100 μmol/m²/s). Unless otherwise noted, all the operations, including axenic sampling during the experiments, were conducted in a sterile particle-free laminar flow hood.

**Nonaxenic cultures with addition of bacteria**

To examine whether or not the presence of bacteria would change the effects of Al on organic carbon decomposition in the marine diatom cultures, bacteria were introduced into the axenic cultures of *T. weissflogii* in the experimental media, when POC in the media had reached a peak. Specifically, axenic cultures of *T. weissflogii* in experimental media (with 0, 40, and 200 nM dissolved Al, respectively) spiked with NaH14CO3 were prepared in the same manner as the axenic experiments. Samples for PO14C were collected and measured as above to monitor the evolution of POC in the cultures. When POC in the cultures had reached a peak, 30 μL of seawater with a bacteria count of 1.9 ± 0.3 × 106 cells/mL was added to introduce bacteria to the cultures (to reach an initial abundance of 1.1 × 104 cells/mL). The seawater with bacteria was collected from an aquarium for keeping live lobsters in a supermarket (Metro) near the INRS laboratory. Bacteria in the aquarium seawater were measured by flow cytometry (BD FACSCalibur) after dyeing the seawater in BD Trucount™ tubes with SYBER-Green I. Samples for DO14C in the cultures during the decay phase were also collected and measured as in the axenic experiments. Similar to the above axenic experiments, all the cultures were kept at 20°C under constant illumination (100 μmol/m²/s), and all the sampling was conducted in a sterile particle-free laminar flow hood.

**Calculation and data analysis**

Cellular carbon content (pmol C/cell) and cellular carbon density (POC per biovolume; pmol C/μm3) were calculated by dividing the amount of POC by total cell abundance and total cell biovolume, respectively. Decomposition rates of POC (d−1) were calculated as the slope of the linear regression of natural logarithms of POC in the media with time (d). Decrease rates (d−1) of cellular carbon content and cellular carbon density, increase rates of DOC in the media during the decay phase, and rates of change in mean cell size were calculated by using the same method as above.
The POC decomposition was divided into different stages if an apparent decrease in the decomposition rates occurred during the decay phase. Decomposition rates of POC in the first stage were used for the comparison among diatom species.

One-way ANOVA followed by least-significant-difference pairwise comparisons and t-tests were used to compare mean values among/between treatments using SPSS 17.0 software (SPSS Inc.) (Field 2009). Data are presented as means or means ± standard deviation.

Results

Effect of Al on the net carbon fixation by *T. weissflogii*

The addition of Al enhanced net carbon fixation by *T. weissflogii* in the experimental media. Higher values for cell abundance, total cell biovolume and POC of *T. weissflogii* were observed in the Al-enriched treatments compared to the control (Fig. 2a–c; Table 1). The amount of POC was significantly higher in the Al-enriched treatments compared to the control throughout the incubation, which lasted more than 64 d (Fig. 2c). Peak POC (final net carbon fixation) (on day 7) increased by 15% ± 6% (*p* = 0.014), 23% ± 8% (*p* = 0.001), and 18% ± 1% (*p* = 0.003) in the treatments enriched with 40, 200, and 2000 nM Al, respectively (Fig. 2c). Peak cell abundance (on day 7) increased by 5% ± 0% (*p* = 0.16), 3% ± 3% (*p* = 0.41), and 7% ± 1% (*p* = 0.10) in the treatments enriched with 40, 200, and 2000 nM Al, respectively (Fig. 2a). Peak values for total cell biovolume (on day 7) increased by 8% ± 0% (*p* = 0.081), 13% ± 0% (*p* = 0.017), and 27% ± 1% (*p* = 0.004) in the treatments enriched with 40, 200, and 2000 nM Al, respectively (Fig. 2b).

Significantly higher growth rates were also observed in terms of abundance (ANOVA, *df* = 7, *p* < 0.05), biovolume (ANOVA, *df* = 7, *p* < 0.01), and POC (ANOVA, *df* = 10, *p* < 0.05) (Fig. S1a). These were consistent with the higher accumulation of diatom biomass in terms of cell abundance, total cell biovolume and POC in the Al-enriched treatments compared to the control (Fig. 2a–c; Table 1). Note, these higher growth rates were observed only in the declining growth phase (or early stationary phase; from the end of the exponential phase when the growth rate starts to slow down to the start of the stationary phase when the growth rate approaches zero, i.e., from day 3 to day 7; Fig. S1b; Pires 2015). The growth rates in the exponential phase were not different among treatments (Fig. S1b).

The DOC concentrations in the media were relatively constant at low levels from day 3 to day 16, and the DOC concentrations in all treatments increased after day 16 (Fig. 2d). There were no significant differences in the DOC concentrations among treatments on both day 3 and day 5 (ANOVA, *df* = 10, *p* > 1.0) (Fig. S2). Higher DOC concentrations were observed in the treatments with higher Al concentrations on day 7 (ANOVA, *df* = 10, *p* < 0.05) and day 16 (ANOVA, *df* = 10, *p* = 0.08). However, concentrations of DOC were significantly lower in the Al-enriched treatments compared to the control on day 25 and day 34 (ANOVA, *df* = 10, *p* < 0.01; Figs. 2d, S2).

Cellular carbon content (pmol C/cell) and cellular carbon density (pmol C/μm³) increased with the accumulation of diatom biomass from day 3 to day 7 (Fig. 2e,f). Significantly higher cellular carbon content, cellular carbon density, and total POC were observed at the end of exponential phase (day 3) in the Al-enriched treatments compared to the control (Figs. 2e,f, S3). Higher cellular carbon content in the Al-enriched treatments compared to the control was observed throughout the experiment (Fig. 2e); the differences in cellular carbon density among treatments became nonsignificant in the declining growth phase, but higher cellular carbon density in the Al-enriched treatments compared to the control was observed again after the declining growth phase (Fig. 2f).

Effect of Al on the decomposition of organic carbon derived from *T. weissflogii*

The results showed that addition of Al significantly slowed down the decomposition rate of *T. weissflogii*-produced POC. After the POC peak, not only the total amount of POC, but also the cellular carbon content and cellular carbon density decreased quickly during the decay phase (Fig. 2c,e,f). Note that the decay phase of POC started from day 7, differing from the decay phase identified based on cell abundance, which started on day 16 (Fig. S1b). To make it clearer, we will call the overlapping period from day 7 to day 16, that is, the stationary phase based on cell abundance, the early decay phase; all references to “decay phase” in the rest of the text are based on POC.

The POC decomposition rates, during the first stage of the decay phase from day 7 to day 34, decreased by 29% ± 4% (*p* = 0.001), 58% ± 10% (*p* < 0.001), and 58% ± 1% (*p* < 0.001) in the treatments enriched with 40, 200, and 2000 nM Al compared to the control, respectively (Table 1). In the control and in two of the three treatments, the POC decomposition rate initially increased and then slowed down quickly (Fig. 3a). The time for the decomposition rate to reach a peak was apparently longer in the Al-enriched treatments compared to the control. In addition, the highest decomposition rates in the Al-enriched treatments were lower than the peak decomposition rate in the control. Thus, there were two apparent stages in the decomposition of *T. weissflogii*-produced POC. The first stage with high decomposition rates (e.g., 0.030 ± 0.000 d⁻¹ in the control) was from day 7 to day 34. The period after the apparent slowing down of the POC decomposition rate was the second stage of the decay (Fig. 3a). The second stage with low decomposition rates (e.g., 0.005 ± 0.001 d⁻¹ in the control) was from day 34 to day 64 (Table 1).

The rates (d⁻¹) of decrease in cellular carbon content and cellular carbon density during the decay phase were significantly lower in the Al-enriched treatments compared to control (ANOVA, *df* = 10, *p* < 0.01) (Fig. 3b, Table 1). Cells of
T. weissflögii showed a decrease in their cellular carbon content and cellular carbon density, while maintaining their abundances in the media during the early decay phase (equivalent to the stationary phase based on cell abundance) from day 7 to day 16 (Fig. 2a,e,f). In this period, the decrease rates (d⁻¹) were up to 69% lower (p < 0.001) in the Al-enriched treatments compared to the control. During the decay phase from day 7 to day 25, the addition of 40, 200, and 2000 nM Al lowered the rates (d⁻¹) of decrease in cellular carbon content by 65% ± 5% (p = 0.001), 45% ± 18% (p = 0.003) and 44% ± 4% (p = 0.004), respectively and the rates of decrease in cellular carbon density by 51% ± 3% (p < 0.001), 58% ± 10% (p < 0.001), and 57% ± 2% (p < 0.001), respectively.

Concurrently with the decomposition and decrease of POC, the amount of DOC increased in the media. During the early decay phase from day 7 to day 16, DOC concentration in all the treatments slightly increased from 19.4 ± 3.3 to 22.0 ± 2.1 μmol C/mL (paired t-test, df = 10, p < 0.001). However, after day 16, DOC concentrations increased significantly in all the treatments (Fig. 2d). From day 7 to day 34 in the decay phase, the DOC increase rates were lower in the Al-enriched treatments compared to the control (ANOVA, df = 10, p < 0.01, Fig. 3c; Table 1). These values were consistent with the lower POC decomposition rates in the Al-enriched treatments compared to the control during the same decay phase (Fig. 3a; Table 1).
Table 1. Comparison of net carbon fixation, carbon decomposition and related parameters in the cultures of *Thalassiosira weissflogii* in Aquil* media with different concentrations of added dissolved Al.

| Parameters                                      | Time/period | Control           | 40 nM          | 200 nM         | 2000 nM        |
|-------------------------------------------------|-------------|-------------------|----------------|----------------|----------------|
| Peak POC (μmol C/mL)                            | Day 7       | 210.9 ± 3.6 (*n* = 3) | 242.6 ± 13.2 (*n* = 2) | 260.4 ± 17.0 (*n* = 3)** | 249.0 ± 1.6 (*n* = 3)** |
| Peak cell abundance (10^3 cells/mL)             | Day 7       | 11.7 ± 0.6 (*n* = 2) | 12.3 ± 0.0 (*n* = 2) | 12.0 ± 0.4 (*n* = 2) | 12.5 ± 0.1 (*n* = 2)** |
| Peak cell biovolume (10^6 fl/mL)                | Day 7       | 87.0 ± 5.6 (*n* = 2) | 93.5 ± 0.4 (*n* = 2) | 98.1 ± 0.1 (*n* = 2)* | 110.7 ± 0.7 (*n* = 2)** |
| Growth rate based on cell abundance             | Days 3–7    | 0.163 ± 0.010 (*n* = 2) | 0.176 ± 0.008 (*n* = 2) | 0.193 ± 0.004 (*n* = 2) | 0.205 ± 0.014 (*n* = 2)* |
| Growth rate based on cell biovolume              | Days 3–7    | 0.072 ± 0.008 (*n* = 2) | 0.100 ± 0.010 (*n* = 2)* | 0.130 ± 0.002 (*n* = 2)** | 0.165 ± 0.015 (*n* = 2)** |
| Growth rate based on POC                        | Days 3–7    | 0.234 ± 0.010 (*n* = 3) | 0.245 ± 0.001 (*n* = 2) | 0.272 ± 0.015 (*n* = 3)** | 0.264 ± 0.016 (*n* = 3)* |
| POC decomposition rate                          | Days 7–34   | 0.030 ± 0.000 (*n* = 3) | 0.021 ± 0.001 (*n* = 2)** | 0.012 ± 0.003 (*n* = 3)** | 0.013 ± 0.000 (*n* = 3)** |
| POC decomposition rate                          | Days 34–64  | 0.005 ± 0.001 (*n* = 3) | 0.006 ± 0.000 (*n* = 2) | 0.006 ± 0.000 (*n* = 3) | 0.011 ± 0.000 (*n* = 3)** |
| DOC increase rate                               | Days 7–34   | 0.061 ± 0.005 (*n* = 3) | 0.055 ± 0.000 (*n* = 2) | 0.044 ± 0.006 (*n* = 3)** | 0.032 ± 0.001 (*n* = 3)** |
| DOC increase rate                               | Days 34–64  | 0.006 ± 0.001 (*n* = 3) | 0.011 ± 0.001 (*n* = 2)** | 0.016 ± 0.002 (*n* = 3)** | 0.021 ± 0.004 (*n* = 3)** |
| Rate of decrease in cellular carbon content     | Days 7–16   | 0.030 ± 0.000 (*n* = 3) | 0.021 ± 0.001 (*n* = 2)** | 0.012 ± 0.003 (*n* = 3)** | 0.013 ± 0.000 (*n* = 3)** |
| Rate of decrease in cellular carbon density     | Days 7–16   | 0.033 ± 0.005 (*n* = 3) | 0.012 ± 0.001 (*n* = 2)** | 0.021 ± 0.006 (*n* = 3) | 0.010 ± 0.001 (*n* = 3)** |
| Rate of decrease in cellular carbon content     | Days 7–25   | 0.022 ± 0.003 (*n* = 3) | 0.007 ± 0.001 (*n* = 2)** | 0.012 ± 0.004 (*n* = 3)** | 0.012 ± 0.001 (*n* = 3)** |
| Rate of decrease in cellular carbon density     | Days 7–25   | 0.040 ± 0.003 (*n* = 3) | 0.020 ± 0.001 (*n* = 2)** | 0.017 ± 0.004 (*n* = 3)** | 0.017 ± 0.001 (*n* = 3)** |
| Rate of decrease in mean cell size              | Days 2–6    | 0.038 ± 0.004 (*n* = 2) | 0.035 ± 0.000 (*n* = 2) | 0.030 ± 0.001 (*n* = 2) | 0.024 ± 0.002 (*n* = 2)** |
| Rate of increase in mean cell size              | Days 7–16   | 0.006 ± 0.001 (*n* = 2) | 0.004 ± 0.000 (*n* = 2) | 0.003 ± 0.001 (*n* = 2) | 0.003 ± 0.001 (*n* = 2)** |

Notes: The rates are expressed in the units of d\(^{-1}\). The data are shown as means ± standard deviation; *n* indicates the number of replicates. POC, particulate organic carbon; DOC, dissolved organic carbon. The symbols #, *, ** in superscripts indicates nearly significant (0.05 < *p* < 0.1), significant (*p* < 0.05) and highly significant (*p* < 0.01) differences compared to the control, respectively. Days 3–7 were in the declining growth phase.

The POC decomposition rates decreased significantly during the second stage (from day 34 to day 64) of the decay phase (Fig. 3a; Table 1): from 0.030 to 0.005 d\(^{-1}\) in the control, and from 0.021 to 0.006 d\(^{-1}\), 0.012 to 0.006 d\(^{-1}\), and 0.013 to 0.011 d\(^{-1}\) in the treatments enriched with 40, 200, and 2000 nM Al, respectively. Significantly higher increase rates of DOC were observed in the Al-enriched treatments compared to the control during the second stage (ANOVA, *df* = 10, *p* < 0.01). This observation is consistent with the relatively higher decomposition rates of POC in the Al-enriched treatments during the same stage (ANOVA, *df* = 10, *p* < 0.01) (Fig. S4a). As a result, the differences in DOC concentrations among treatments had disappeared at the end of this stage (ANOVA, *df* = 10, *p* > 0.1), whereas the amounts of POC were still significantly higher in the Al-enriched treatments compared to the control (ANOVA, *df* = 10, *p* < 0.01) (Fig. S4b). Significant correlations were observed between the POC decomposition rate and DOC increase rate (Fig. 3d). During the whole decay phase from day 7 to day 64, the POC decomposition rate explained 62% of the DOC increase rate (*df* = 43, *R*\(^2\) = 0.62, *p* < 0.0001), and the increased amount of DOC (84.1 ± 5.4 μmol C/mL) was about 72 ± 8% on average of the decreased amount of POC (118.4 ± 11.7 μmol C/mL) (Fig. S5). During the early decay phase from days 7–16, only...
49.5% of the DOC increase rate was explained by the POC decomposition rate \((\text{df} = 10, R^2 = 0.495, p < 0.05)\), and the increased amount of DOC \((2.5 \pm 1.6 \mu\text{mol C/mL})\) was only \(13 \pm 9\%\) on average of the decreased amount of POC \((21.7 \pm 14.3 \mu\text{mol C/mL})\) (Fig. S5). The regression lines describing the correlations showed that one unit increase in POC decomposition rate would lead to \(0.87\) unit increase in DOC increase rate during the early decay phase \((y = 0.87x + 0.005)\), whereas during the whole decay phase one unit increase in POC decomposition rate would lead to \(2.21\) units increase in DOC increase rate \((y = 2.21x + 0.005)\). These results indicate that the early decay phase was characterized by greater respiration than the decay phase as a whole.

**Effect of Al on the mean cell size and cell size distribution of *T. weissflogii***

Significantly larger mean diatom cell sizes were observed in the Al-enriched treatments compared to the control (Fig. 4a). Mean cell size (in diameter) of *T. weissflogii* decreased quickly with the accumulation of diatom biomass (expressed as cell abundance and POC) until the end of the declining growth phase (on day 7) (Figs. 2a, 4a). The rates of decrease in mean diatom cell size were significantly higher in the control, and lower rates were observed in treatments with higher Al concentrations (ANOVA, \(df = 7, p < 0.01\)) (Fig. S6a; Table 1). As a result, significantly higher mean diatom cell sizes were observed in the Al-enriched treatments after the exponential phase (ANOVA, \(df = 7, p < 0.05\)) (Fig. 4a). The results of cell size distribution measurements also showed that a higher proportion of larger diatom cells occurred in Al-enriched treatments compared to the control, and the differences became more and more apparent with the accumulation of diatom biomass (Figs. 2a, 4b, S6).

In addition, during the decay phase lower rates of increase in mean diatom cell size and delayed cell lysis were observed in the Al-enriched treatments compared to the control. The mean diatom cell size increased again during the early decay phase, and finally the cells broke down at the late decay phase. During the early decay phase (day 7 to day 16), the diatom cells remained intact and the cell abundances of the diatom kept relatively constant in all the treatments (Figs. 2a, S6). During this period, the rates of increase in mean diatom cell size were significantly higher (ANOVA, \(df = 7, p < 0.05\)) in the control.
compared to the Al-enriched treatments (Fig. S6b; Table 1). As the decay progressed with time, we observed on day 25 a peak of small debris (~8 μm in diameter), which was more pronounced in the control compared to the Al-enriched treatments (Fig. 4c). As a result, higher cell abundances were observed in the treatments with higher concentrations of Al on day 25 (Fig. 2a). In the late decay phase on day 34, almost all the diatom cells had broken down (degenerated) into debris in the control, whereas a large proportion of the diatom cells remained intact as large particles in the Al-enriched treatments (Fig. 4d).

Effect of Al on the net carbon fixation and decomposition of T. pseudonana and T. oceanica

Higher net carbon fixation and lower decomposition rates of POC produced by T. pseudonana and T. oceanica were observed in the Al-enriched treatments compared to the controls (Table 2). Peak POC concentrations (final net carbon fixation; on day 7) produced by T. pseudonana were 9% ± 7% (p = 0.07) and 29% ± 4% (p < 0.001) higher in treatments enriched with 40 and 200 nM Al, respectively, compared to the control (Fig. 5a). Peak POC concentrations (final net carbon fixation; on day 13) produced by T. oceanica were 15% ± 6% (p = 0.016) and 20% ± 6% (p = 0.003) higher in treatments enriched with 40 and 200 nM Al, respectively (Fig. 5b). Similar to what we observed for T. weissflorigii, significantly higher rates of POC accumulation were observed in the Al-enriched treatments compared to the control for T. pseudonana, but not for T. oceanica, during the declining growth phase (Fig. S7).

Different phases of the decomposition of T. pseudonana-produced POC were observed in the treatments enriched with different concentrations of Al. In the control and in the treatment enriched with 40 nM Al, the POC decomposition rates decreased with decay time, and the decomposition of T. pseudonana-produced POC could be divided into three stages: the first stage from day 7 to day 10 (with a decomposition rate of 0.165 ± 0.018 d⁻¹ in the control), the second stage from day 10 to day 17 (with a decomposition rate of 0.079 ± 0.009 d⁻¹ in the control) and the third stage from day 17 to day 24 (with a decomposition rate of 0.072 ± 0.004 d⁻¹) (Fig. S8a). Therefore, there were only two decomposition stages for the decomposition of T. pseudonana-produced POC in the treatment enriched with 200 nM Al, with the first stage lasting from day 7 to day 17 (with a decomposition rate of 0.072 ± 0.004 d⁻¹) and the second stage following day 17 (Figs. 5a, S8a).

Distinct phases of the decomposition of T. oceanica-produced POC were also observed in the treatments enriched with different concentrations of Al. For the control, the
decomposition rate decreased slightly from 0.058 ± 0.007 d⁻¹ during days 13–17 to 0.049 ± 0.008 d⁻¹ during days 17–24, and then decreased significantly to 0.027 ± 0.010 d⁻¹ during days 24–31 (Fig. S8b). For the Al-enriched treatments, the POC decomposition rates increased from low values during days 13–17 (0.037 and 0.019 d⁻¹ in the treatments enriched with 40 and 200 nM Al, respectively) to high values during days 17–24, and then decreased to low values during days 24–31 (0.021 and 0.030 d⁻¹ in the treatments enriched with 40 and 200 nM Al, respectively) (Fig. S8b). Therefore, for all the treatments, the decomposition of *T. oceanica*-produced POC could be divided into two stages: the first stage from day 13 to day 17 and the second stage from day 17 to day 24.

### Table 2. Comparison of net carbon fixation and carbon decomposition in the cultures of *T. pseudonana* (TP), *T. oceanica* (TO) and *T. weissflogii* (TW) in Aquil* media with different concentrations of added dissolved Al.

| Parameters | Time/period | Control | 40 nM | 200 nM |
|------------|-------------|---------|-------|--------|
| Peak POC in axenic cultures of TP (μmol C/mL) | Day 7 | 359.4 ± 7.8 (n = 3) | 392.6 ± 26.9 (n = 2) | 464.0 ± 14.2 (n = 3) |
| Peak POC in axenic cultures of TO (μmol C/mL) | Day 13 | 212.0 ± 2.9 (n = 3) | 243.7 ± 12.6 (n = 2) | 253.7 ± 12.1 (n = 3) |
| Decomposition rates of POC in axenic cultures of TP (d⁻¹) | Days 7–10 | 0.165 ± 0.018 (n = 3) | 0.130 ± 0.012 (n = 2) | 0.072 ± 0.004 (n = 3) |
| Decomposition rates of POC in axenic cultures of TO (d⁻¹) | Days 13–24 | 0.052 ± 0.004 (n = 3) | 0.052 ± 0.004 (n = 2) | 0.031 ± 0.001 (n = 3) |
| Decomposition rates of POC in axenic cultures of TW (d⁻¹) | Days 7–25 | 0.030 ± 0.003 (n = 3) | 0.014 ± 0.001 (n = 2) | 0.012 ± 0.004 (n = 3) |
| Decomposition rates of POC in nonaxenic cultures of TW (d⁻¹) | Days 7–23 | 0.071 ± 0.003 (n = 3) | 0.045 ± 0.005 (n = 2) | 0.044 ± 0.008 (n = 3) |

Notes: The data are shown as mean ± standard deviation; n indicates the number of replicates. The symbols #, *, ** in superscripts indicates nearly significant (0.05 < p < 0.1), significant (p < 0.05) and highly significant (p < 0.01) differences compared to the control, respectively.

### Fig. 5. POC and DOC in the cultures of (a, c) *T. pseudonana* and (b, d) *T. oceanica* in Aquil* media with different Al concentrations. The error bars represent standard deviation (n = 2 or 3). The symbols * and ** in subfigures (c) and (d) show the differences between/among the treatments were significant (p < 0.05) and highly significant (p < 0.01), respectively.
24, and a second stage from day 24 to day 31 (Figs. S5b, S8b). Along with the decomposition of POC during the decay phase, DOC concentrations in both the cultures of *T. pseudonana* and *T. oceanica* increased with time (paired *t*-test, df = 7, *p* < 0.001) (Fig. 5c,d).

Significantly higher decomposition rates of POC during the first stage of the decay phase were observed in the control compared to the Al-enriched treatments, for both *T. pseudonana* and *T. oceanica* as well as *T. weissflogii* (Fig. 6a, Table 2). The decomposition rates of *T. oceanica*-produced POC decreased by 0 and 41% ± 3% (*p* = 0.001) in the treatments enriched with 40 and 200 nM Al, respectively. The decomposition rates of *T. pseudonana*-produced POC decreased by 22% ± 7% (*p* = 0.031) and 57% ± 3% (*p* < 0.001) in the treatments enriched with 40 and 200 nM Al, respectively. Taking all three diatoms together, the POC decomposition rates decreased exponentially along with an increase of mean cell size (Fig. 6b). The results showed that Al changed the relationship between the POC decomposition rates with mean cell size. For example, the scaling factor for the natural exponential function decreased from −0.895 to −0.579 as the Al concentrations increased from 0 to 200 nM (Fig. 6b). In addition, the constant factor in the equation decreased (from 0.0295 to 0.0118) with the increase of Al concentrations. These differences indicate how Al could affect the decomposition rate of POC produced by marine diatoms with different cell sizes.

**Effects of Al on the carbon decomposition of *T. weissflogii* in nonaxenic cultures**

In the nonaxenic cultures, significantly lower POC decomposition rates were also observed in Al-enriched treatments compared to the control. After the introduction of bacteria to the experimental media (on day 7), POC in all the treatments decreased rapidly with time (Fig. 7a). The presence of bacteria significantly increased the POC decomposition in all the treatments. Similar to what was observed in the axenic cultures, POC decomposition rates in the nonaxenic cultures increased with time during the decay phase from day 7 to day 23 (Fig. 7b). However, the POC decomposition rates in the nonaxenic cultures were more than two times higher than those in the axenic cultures (Fig. 7c). Similar differences in POC decomposition rates between nonaxenic cultures and axenic cultures were observed at different stages (days 7–16 and days 16–25) of the decay phase (Fig. 59). Despite the increase in overall POC decomposition in the nonaxenic cultures, the addition of Al still significantly slowed down the decomposition process. The POC decomposition rates in the treatments enriched with 40 and 200 nM Al decreased by 37% ± 7% (*p* = 0.004) and 38% ± 11% (*p* = 0.002), respectively (Fig. 7c).

Along with the accelerated decomposition of POC, DOC concentrations in all the nonaxenic cultures on day 16 were about seven times higher than those in the axenic cultures at the same period (Figs. 2d, 7d). In contrast with the axenic experiments, we did not observe significantly higher concentrations of DOC in the control compared to the Al-enriched treatments during the decay phase (Fig. 7d). No significant increase (accumulation) in the DOC concentrations was observed during the decay process (from day 16 to day 23). On the contrary, the DOC concentrations in the control and in the treatment enriched with 40 nM Al decreased significantly (paired *t*-test, df = 4, *p* < 0.05) from day 16 to day 23 (Fig. 7d).

In fact, the decrease in POC (81.3 ± 14.5 μmol C/mL) during days 16–23 in the nonaxenic cultures was greater than that during the days 16–25 in the axenic cultures (37.8 ± 14.8 μmol C/mL) (Fig. S10). For the axenic cultures, the increase in DOC (15.8 ± 5.9 μmol C/mL) was about...
43 ± 8% of the decrease in POC. In contrast, DOC decreased in the nonaxenic cultures during days 16–25, indicating enhanced consumption of DOC by bacteria (Fig. S10).

**Discussion**

The present study indicates that Al can not only enhance net carbon fixation by the three marine diatoms, but also significantly slow down the decomposition of the diatom-produced POC. Our results also show that addition of Al increased the diatom cell size, cellular carbon content, and cellular carbon density during the growth period. In addition, Al slowed down the loss of cellular carbon content and cellular carbon density during the early decay phase, and decreased the breaking down of diatom cells into debris and the transformation of POC to DOC during the late decay phase. These observations provide additional evidence for the iron–aluminum hypothesis, which suggests that Al can increase carbon fixation in the upper ocean and reduce the decomposition of organic carbon produced by marine organisms, especially marine phytoplankton. In doing so, Al could influence climate change by enhancing carbon export and sequestration in ocean depths and drawing down atmospheric CO₂ (Zhou et al. 2018b).

**Beneficial effects of Al on the growth and carbon fixation of marine phytoplankton**

The enhanced net carbon fixation by the marine diatoms *T. weissflogii*, *T. pseudonana* and *T. oceanica* in the Al-enriched treatments, compared to the controls, is consistent with previous reports of the beneficial effects of Al on the growth of marine phytoplankton (Shi et al. 2015; Zhou et al. 2016; Liu et al. 2018; Zhou et al. 2018a). The previous studies showed that Al enhanced the yield of phytoplankton biomass in terms of cell abundance, total cell volume, photosynthetic pigments (i.e., chlorophyll *a*) and nitrogen fixation. The present study adds to these earlier results and provides direct evidence to show that Al was beneficial to the growth of marine diatoms in terms of carbon fixation. The beneficial effect of Al addition on *T. weissflogii* was evidenced by larger cell sizes and increased organic carbon content, but not by increased cell abundance (Table 1). Also consistent with previous reports, significantly higher growth rates of marine diatoms were observed in the Al-enriched treatments compared to the control, during the declining growth phase (Figs. S1, S7).
The higher growth rates observed in the Al-enriched treatments during this phase, when phosphorus limitation occurred, are likely related to the proposed mechanism of Al-facilitated DOP utilization (Zhou et al. 2016; Fig.1). The diatoms may also use polyphosphate bond to the internalized Al in diatom cells, as our recent study showed that most (69%) of the internalized Al in T. weissflogii cells was bound as inorganic granules, likely in polyphosphate bodies (Liu et al. 2019).

Aluminum may influence the growth of marine phytoplankton through other mechanisms. The present study for the first time showed that addition of Al (at levels of 40–2000 nM) could significantly increase the cellular carbon content (by 11%–15%) and cellular carbon density (by 16%–17%) of the marine diatom T. weissflogii, even during the exponential growth phase (Fig. S3) when the diatom growth was presumably not limited by nutrients. In fact, beneficial effects of Al on the growth of marine phytoplankton have also been observed in phosphorus-sufficient media in previous studies (Şaçan et al. 2007; Golding et al. 2015; Gillmore et al. 2016). However, the mechanisms for the beneficial effects of Al were not discussed in the previous studies. In early studies, Al was suggested to have a catalytic effect on the growth of marine phytoplankton, especially diatoms (Menzel et al. 1963; Stoffyn 1979). However, no subsequent study revisited the catalytic effect of Al until recent years (Shi et al. 2015; Zhou et al. 2016). Both the results in the present study and those in previous studies indicate that Al may enhance the growth of marine phytoplankton (including diatoms) through other mechanisms, in addition to enhancing the utilization of organically bound phosphorus. Previous studies have shown that the marine diatom T. weissflogii can internalize substantial Al into its intracellular environment, including organelles (e.g., perhaps into the chloroplast) (Liu et al. 2019), and Al treatment could increase the cellular chlorophyll content of marine phytoplankton (including T. weissflogii) (Shi et al. 2015; Zhou et al. 2016). Enhanced photosynthesis has been suggested as an explanation of Al-induced growth stimulation in tea plants, as Al supply increased the chlorophyll a concentrations and net assimilation rates of CO₂ in tea plant leaves (Hajiboland et al. 2013). The enhanced carbon fixation and higher cellular carbon content and cellular carbon density in the Al-enriched treatments compared to the control in the present study (Fig. 2) were possibly related to enhanced photosynthesis. However, no established biological role for Al has yet been reported (Exley and Mold 2015). Further studies, for example, short-term assays of 14C uptake by Al-treated diatom cells in different growth phases, undoubtedly are needed to explore the mechanisms that underlie the beneficial effects of Al on the growth and carbon fixation of marine phytoplankton.

Possible mechanisms for the Al effects on reducing the decomposition rate of POC

The present study indicates that Al can slow down the decomposition of diatom-produced POC and the transformation of POC to DOC, not only by lowering rates at which cellular carbon content and cellular carbon density decrease during the early decay phase (Fig. 3), but also by delaying the breaking down (lysis) of the intact cells during the late decay phase (Fig. 4). These results indicate that Al may reduce the decomposition rate of diatom-produced POC through different mechanisms.

Incorporation of Al into organic molecules and diatom cells may decrease the rate at which the organic carbon is degraded. First, some of the Al taken up by diatoms is assimilated into their frustules. This incorporation can reduce the dissolution rate of the frustule, and potentially reduce the degradation rate of the frustule-associated organic carbon (Abramson et al. 2009). Second, Al can react with biomolecules in biological systems to form strong bonds and structures (Song et al. 2014; Exley and Mold 2015; Mujika et al. 2018), which are potentially difficult to dissociate and decompose (Zhou et al. 2018b). As a result, Al could delay the breaking down (or lysis) of diatom cells and decrease the decomposition rate of the diatom-produced POC.

Aluminum may delay cell death and lysis of marine diatoms by alleviating phosphorus depletion. Phosphate (100 nM) was low compared to other nutrients such as nitrate (100 μM) and silicate (100 μM) in the experimental media. Phosphate should be the first nutrient to be depleted in the media. Depletion of nutrients such as phosphorus can lead to diatom cell death and lysis (Bidle 2015; Rokitta et al. 2016; Wang et al. 2020). Our previous studies show that the marine diatom T. weissflogii can live longer in the Al-enriched media compared to the control (Zhou et al. 2016). Similar to the previous study, in the present study lower rates of increase in mean cell size (indicating cell swelling) and lower decrease rates of cellular carbon content and cellular carbon density were observed in the Al-enriched treatments compared to the control (Figs. 3b; 4a). In addition, delayed breaking down of the diatom cells was observed in the Al-enriched treatments compared to the control (Fig. 4c,d). These results indicate that Al may delay the senescence, death and lysis of marine diatoms caused by phosphorus depletion. We speculate that besides increasing the net carbon fixation by marine diatoms during the declining growth phase, the Al-related enhanced utilization of DOP and the possible use of polyphosphate bound to internalized Al in diatom cells may help the cells to cope with phosphorus depletion during the early decay phase (Zhou et al. 2016; Liu et al. 2019). Further work is undoubtedly needed to confirm this speculation.

Our results are consistent with the general appreciation that the decomposition of phytoplankton-produced POC is an important source of DOC in the ocean. Along with decomposition of POC, DOC constantly increased in the axenic media until the end of the experiments (Figs. 2d; 3d; 5c,d), whereas in the nonaxenic media DOC concentrations did not continuously increase but in some cases actually decreased during the decay phase, presumably because of bacterial consumption (Fig. 7c). Similarly, different trends of DOC changes in axenic
and nonaxenic cultures of the marine diatom *Skeletonema costatum* have been reported (Grossart et al. 2006). The significant correlation of the POC decomposition rate with the DOC increase rate further indicates that the diatom-produced POC was released as DOC during the decay phase (Fig. 3d). Our results also showed that the presence of bacteria more than doubled the POC decomposition rates in all the treatments (Figs. 3a, 7b, S9). This is consistent with the observation that bacteria can hasten the transformation of POC to DOC by efficiently removing the organic matrix in diatom frustules and thus promoting silica dissolution (Smith et al. 1992; Bidle and Azam 1999), and by augmenting diatom cell death after the exponential growth phase (Brussaard and Riegman 1998; Grossart and Simon 2007). Our results show that Al can significantly reduce the decomposition rate of diatom-produced POC and the transformation of POC to DOC, regardless of the presence or absence of bacteria in the seawater. Further studies are needed to examine whether Al could influence the decomposition of DOC.

**Implication for carbon export to ocean depths and the iron-aluminum hypothesis**

The present study indicates that Al can increase carbon export to ocean depths by enhancing the efficiency of the biological pump. First, the Al-induced increase of carbon fixation by marine diatoms could provide more particulate carbon in the upper ocean ready for export. Second, the Al effects leading to an increase in the mean cell size and cellular carbon content of marine diatoms could directly contribute to the export of carbon to ocean depths, as larger cells usually have a higher potential to be exported to ocean depths (Waite et al. 1992; Miklasz and Denny 2010; Laurenceau-Cornec et al. 2020). Third, the Al-related reduced decomposition rate of marine diatom-produced POC could also favor an increased export of carbon to deeper depths and subsequent sequestration of carbon in the ocean.

A simple calculation suggests that the supply of Al leads to 2–4 fold increases in the POC exported to 200 m depths, and increases of 1–3 orders of magnitude in the POC exported to 1000 m, respectively (Fig. 8). These approximate calculations simply assume that the initial amount of POC produced by the diatom *T. weissflogii* in surface ocean, the decomposition rate of the diatom-produced POC, and the sinking velocity of the diatom cell are the only three factors determining carbon export to ocean depths. Specifically, the initial amount of POC and the decomposition rates of POC in each scenario are taken from the experiments for *T. weissflogii* (Tables 1 and 2). For example, the initial amounts of POC are assumed to be 100%, 115%, and 123% in the scenarios of Control, 40 nM Al, and 200 nM Al, respectively. The results imply that addition of Al in the upper ocean in the range of 40–200 nM could lead to significant (several orders of magnitude) increase in the amount of POC exported to 1000 m and below.

The concentrations of dissolved Al in the upper ocean are strongly related to dust deposition (Measures and Vink 2000; Kienast et al. 2016; Menzel Barraqueta et al. 2020). Increases in dust deposition during the Last Glacial Maximum compared to the late Holocene (i.e., the modern time) occurred over the world oceans including all the modern high-nutrient low-chlorophyll regions (i.e., the Southern Ocean, the subarctic Pacific, and the Eastern Equatorial Pacific) (Kienast et al. 2016). A two- to three-fold increase in the dust deposition rates over those in modern time may result in increases of Al in the range from 20 to 200 nM in the upper layer for...
the Atlantic Ocean, the Mediterranean Sea, and some sites of the Pacific Ocean and the Indian Ocean (Kienast et al. 2016; Menzel Barraqueta et al. 2020). In other words, Al may have significantly increased carbon export to ocean depths in the Last Glacial Maximum. In addition, a recent study shows that Al may play an important role in preserving carbon in microfossils approximately 800 million years ago (Anderson et al. 2020). However, similar calculations for the Southern Ocean suggest that increases of Al concentrations in glacial times compared to interglacial times in the Southern Ocean would have been less than 10 nM. The Southern Ocean plays an important role in the exchange of carbon between ocean and atmosphere and thus in the climate system (De Angelis et al. 2018b). To examine the hypothesis further, much work both in the laboratory and in the field is needed to test the effects of Al at environmentally relevant low levels (e.g., <20 nM) on marine diatoms and other phytoplankton species.

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Conflict of interest
None declared.