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Strong responses of Southern Ocean phytoplankton communities to volcanic ash

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Key Points:

- Bottle-scale iron and volcanic ash addition experiments were conducted
- Phytoplankton responded more to the ash than iron in a number of experiments
- The ash is suggested to have relieved phytoplankton manganese (co)limitation

Supporting Information:

- Readme
- Text S1, Tables S1–S3, and Figure S1

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Abstract Volcanic eruptions have been hypothesized as an iron supply mechanism for phytoplankton blooms; however, little direct evidence of stimulatory responses has been obtained in the field. Here we present the results of twenty-one 1–2 day bottle enrichment experiments from cruises in the South Atlantic and Southern Ocean which conclusively demonstrated a photophysiological and biomass stimulation of phytoplankton communities following supply of basaltic or rhyolitic volcanic ash. Furthermore, experiments in the Southern Ocean demonstrated significant phytoplankton community responses to volcanic ash supply in the absence of responses to addition of dissolved iron alone. At these sites, dissolved manganese concentrations were among the lowest ever measured in seawater, and we therefore suggest that the enhanced response to ash may have been a result of the relief of manganese (co)limitation. Our results imply that volcanic ash deposition events could trigger extensive phytoplankton blooms, potentially capable of significant impacts on regional carbon cycling.

1. Introduction

Phytoplankton growth in the high-nitrate low-chlorophyll (HNLC) regions of the world's oceans is limited by the availability of iron (Fe) [*Boyd et al.*, 2007]. Experiments that have artificially supplied Fe to HNLC waters triggered significant phytoplankton responses, typically including the following: an increase in overall biomass, an increased apparent efficiency of photochemical energy conversion (F_v/F_m), and a shift in the species composition of phytoplankton toward a diatom-dominated community [*Boyd et al.*, 2007]. This biogeochemical response to Fe fertilization has the potential to sequester CO_2 from the atmosphere into the deep ocean. Although the efficiency of such sequestration remains uncertain, recent studies have suggested that significant carbon export is probable under the right conditions [*Blain et al.*, 2007; *Smetacek et al.*, 2012].

The delivery of volcanic ash to Fe-limited waters has been hypothesized as a natural fertilization mechanism, whereby the dissolution of Fe-rich soluble salts on the surface of ash particles (or possibly the ash itself) supplies Fe and potentially relieves limitation [*Duggen et al.*, 2010]. Volcanic ash fertilization of remote Fe-limited waters was proposed to cause the detected atmospheric CO_2 drawdown after the Pinatubo 1991 eruption as a result of postfertilization increases in marine primary productivity [*Watson*, 1997]. Furthermore, this fertilization mechanism has been hypothesized to drive large-scale perturbations to biogeochemical cycles and climate observed in geological or ice core records [*Bay et al.*, 2004; *Cather et al.*, 2009].

To date, evidence for the volcanic ash fertilization hypothesis has generally relied on either measuring trace metals released from ash [e.g., *Olgun et al.*, 2011, 2013; *Duggen et al.*, 2007; *Achterberg et al.*, 2013], detecting the response of phytoplankton cultured in the laboratory to ash addition [*Duggen et al.*, 2007; *Hoffmann et al.*, 2012], or observing posteruptive phytoplankton blooms using remote sensing [*Hamme et al.*, 2010; *Langmann et al.*, 2010; *Achterberg et al.*, 2013]. Recent results from a bottle-enrichment experiment in the North Atlantic have demonstrated the fertilization potential of Icelandic volcanic ash in a region not normally considered to be a classic HNLC system [*Achterberg et al.*, 2013], while a positive phytoplankton community response to ash addition after a four-day time lag has recently been reported for the HNLC North Pacific [*Mélançon et al.*, 2014]. Until now, however, the response of phytoplankton to ash fertilization in the Southern Ocean, the most biogeochemically significant HNLC system [*Sigman et al.*, 2010], has remained untested. Here we present the results from a suite of Fe and volcanic ash addition

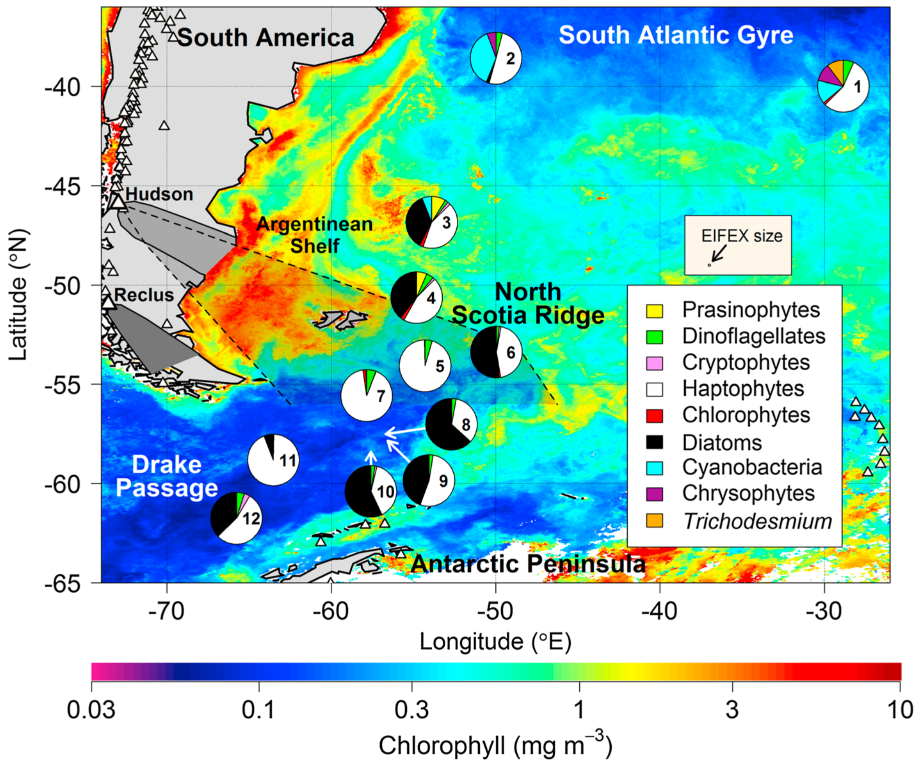

Figure 1. Phytoplankton types and chlorophyll concentrations at experimental sites. Background image shows a January-to-March 2012 satellite composite of chlorophyll concentrations from Moderate Resolution Imaging Spectroradiometer (http://oceancolor.gsfc.nasa.gov/). Overlain pie charts represent the dominant phytoplankton types present in waters at each experimental site. Experiment numbers are labeled. Triangles show the locations of volcanoes thought to have been active in the last 10,000 years (Global Volcanism Program, http://www.volcano.si.edu/index.cfm). To illustrate the potential scale of natural ash additions in this region, volcanic ash deposition from two Quaternary volcanic eruptions are shown (grey-shaded regions enclosed in solid lines): >10 mm isopach (ash thickness) for the Hudson 1991 eruption [*Scasso et al.*, 1994] (light grey); and >30 mm isopach for the ~ 14.8 cal ka B.P. Reclus R1 eruption [*Stern*, 2008; *Fontijn et al.*, 2014] (dark grey). Note that, although likely extending into open ocean waters, no Reclus isopachs (dark grey) have been mapped further south than the region highlighted. The shaded region bounded by the dashed line represents the 15 August 1991 Hudson ash cloud extent from the Total Ozone Mapping Spectrometer aerosol index (http://ozoneaq.gsfc.nasa.gov/index.md). For scale, the size of the 167 km^2 Fe-fertilized patch for the European Iron Fertilization Experiment (EIFEX) is shown by a circle in the inset box.

experiments conducted across a range of oceanic regimes (subtropical gyre, productive shelf, and HNLC waters; see Figure 1). These provide clear evidence for the potential for volcanic ash deposition to stimulate phytoplankton growth in the Southern Ocean.

2. Methods

Incubation experiments were carried out on consecutive cruises in the South Atlantic and Southern Ocean from January to March 2012 (Figure 1 and Tables S1 and S2 in the supporting information). For full method details see supporting information. Briefly, incubation bottles were filled with surface seawater and spiked with either a $FeCl_3$ solution or volcanic ash. Both basaltic (Etna, Sicily 2002 eruption) and rhyolitic (Chaitén, Chile 2008 eruption—sample of *Watt et al.* [2009]) ash was used, with masses of ash added reflecting realistic seawater loading and dilution within a 50 m surface mixed layer (see supporting information). Fertilized bottles were incubated in an environment simulating the upper ocean for 24 h (48 h for experiment 12). Subsequently, bottles were subsampled for phytoplankton photophysiology and chlorophyll concentrations using fluorescence techniques (*Kolber et al.* [1998] and *Holm-Hansen et al.* [1965], respectively). Active chlorophyll fluorescence measurements using Fast Repetition Rate fluorometry were used to calculate the apparent photochemical efficiency of photosystem II (F_v/F_m), providing a sensitive and rapidly responding indication of relief from Fe limitation [*Behrenfeld and Milligan*, 2013].

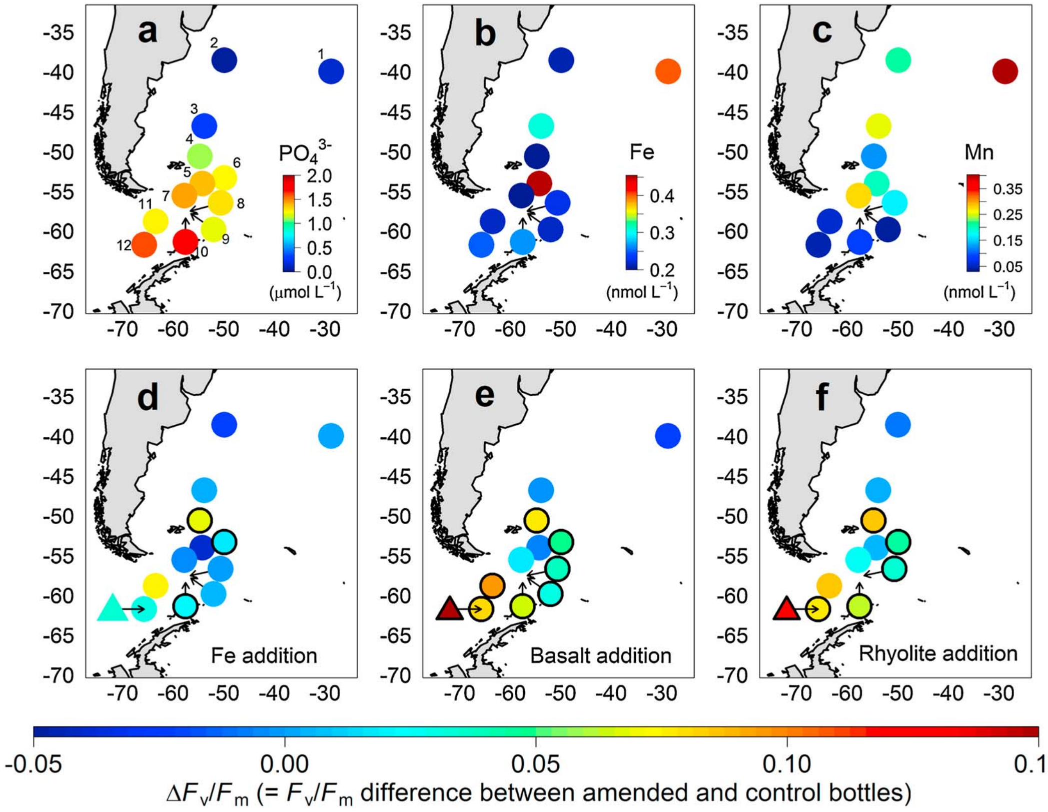

Figure 2. Seawater nutrient concentrations and the response of phytoplankton to iron and ash additions. Dots represent the locations of experiments, with colors representing (a–c) the nutrient concentration or (d–e) the level of phytoplankton response. Experiment numbers are labeled in Figure 2a. Nitrate concentrations showed a strong correlation with phosphate (Figure 2a) ($R^2 = 0.97$; $p < 0.001$). For Figures 2d and 2e: $\Delta F_v/F_m = F_v/F_m$ of waters amended with iron spike (Figure 2d) or ash (Figures 2e and 2f) $-$ F_v/F_m control bottles [*Ryan-Keogh et al.*, 2013]; circular symbols represent the response after 24 h incubation, triangles after 48 h incubation; black outlines around symbols indicate a statistically significant response from amended bottles over control bottles (*t* test $p < 0.05$). Arrows point to the sites of experiments 8–10 and 12 (labeled in Figure 2a).

Measurements on untreated surface-waters characterized the initial nutrient regime and phytoplankton community present. Trace metal micronutrient concentrations were determined by inductively coupled plasma-mass spectrometry following the method of *Milne et al.* [2010], while macronutrient concentrations were determined using a segmented flow colorimetric autoanalyzer [*Woodward and Rees*, 2001]. Phytoplankton community structure was determined by analyzing the accessory pigment composition using high-performance liquid chromatography [*Gibb et al.*, 2000], combined with the CHEMTAX program for assessing the contribution of phytoplankton types to total chlorophyll biomass [*Mackey et al.*, 1996]. Short-duration (2 h) leaching experiments were also conducted using Milli-Q deionized water to characterize the release of trace metals from the two types of ash used. Metals released using such experiments likely represent an upper bound of solubility in seawater due to the more acidic nature of Milli-Q over seawater.

3. Results and Discussion

Initial phytoplankton biomass, community structure, and macronutrient concentrations showed expected patterns for the oceanic provinces encountered. Chlorophyll concentrations increased from the South Atlantic Gyre to the Argentinean Shelf and North Scotia Ridge before declining significantly in the Drake Passage (Figure 1 and Table S1 in the supporting information). Phytoplankton community structure showed a general north-to-south shift from haptophyte-cyanobacteria-dominated communities in gyre waters to haptophyte-diatom-dominated communities in the Southern Ocean (Figure 1). Nitrate and phosphate increased from low, depleted values in gyre waters to much increased values in the Drake Passage (Figure 2a), while silicate increased south of the polar front (Table S1 in the supporting information). Concentrations of the trace metal

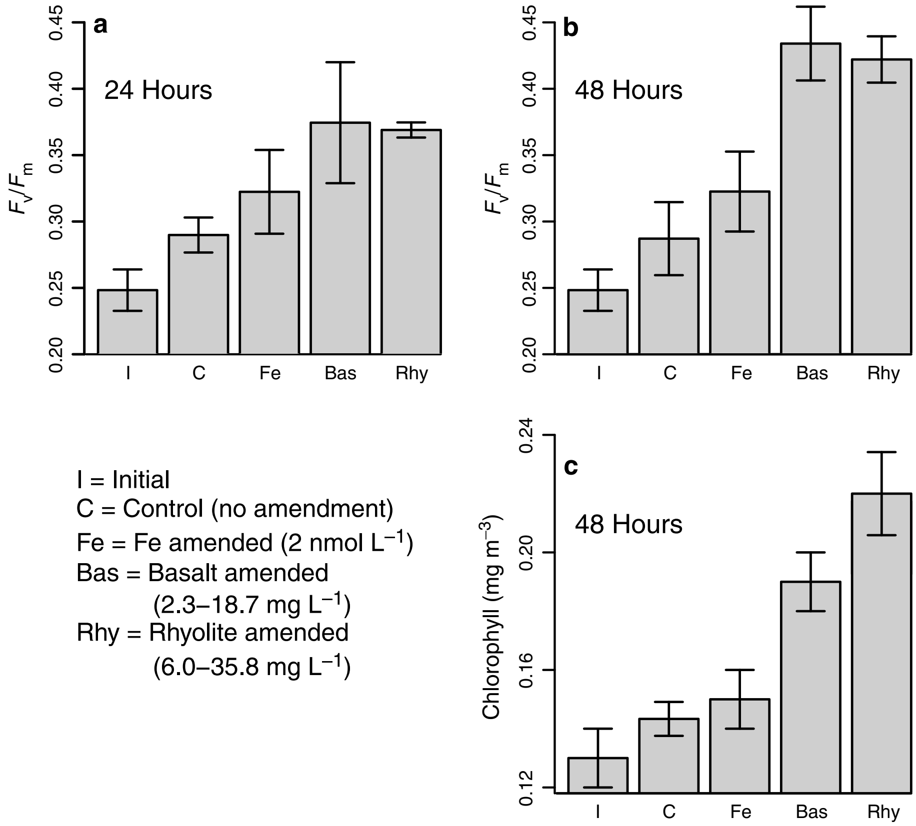

Figure 3. Phytoplankton response to ash addition in Drake Passage (experiment 12): (a and b) the initial photophysiological status and response after 24 and 48 h, respectively; (c) the initial chlorophyll concentration and response after 48 h.

micronutrients Fe and manganese (Mn) generally demonstrated a north-to-south reduction (Figures 2b and 2c and Table S1 in the supporting information). Concentrations of Mn in the surface waters of Drake Passage reached as low as 0.034 nmol L^{-1}, representing some of the lowest values ever measured in seawater, comparable with previous minimal Southern Ocean values (~0.04 nmol L^{-1}) [*Middag et al.*, 2011, 2012, 2013]. Other trace metals of biological importance (Zn, Cu, Ni, and Cd) were at concentrations expected to be in excess of phytoplankton requirements [*Bruland et al.*, 1991] (see Text S1 and Table S1 in the supporting information).

Of the 23 sets of triplicate bottles amended with ash, 18 sets produced statistically significant (t test $p < 0.05$) increases in F_v/F_m relative to control (nonamended) bottles. For the remaining five experiments, located in macronutrient-depleted South Atlantic waters (experiments 1 and 2) and three sites around the Falkland Islands (experiments 3, 5, and 7), there was no response to either Fe or ash addition. In marked contrast to previous experiments performed in the North Atlantic [*Achterberg et al.*, 2013], phytoplankton responses to ash addition were always greater than those in Fe-spiked bottles (Figures 2d–2f and Table S2 in the supporting information). Particularly enhanced responses from phytoplankton amended with ash, relative to those amended only with Fe, were found in the vicinity of Drake Passage (Figures 2d–2f and also see Figure 3)—a region widely assumed to be severely Fe limited [*Martin et al.*, 1990; *Hopkinson et al.*, 2007]—and containing some of the lowest chlorophyll concentrations in the Southern Ocean (<0.1 mg m^{-3}).

In order to limit the potential for confounding taxonomic changes to influence the interpretation of physiological (F_v/F_m) responses [*Suggett et al.*, 2009], experimental durations were typically kept short enough (24 h) to prevent significant increases in biomass (Table S2 in the supporting information). However, within the single experiment run over a longer time scale in Drake Passage, both F_v/F_m and chlorophyll concentrations in the ash-amended bottles increased significantly above that of the control and Fe-amended bottles (Figure 3). Significantly enhanced physiological and growth responses were thus observed for ash-amended phytoplankton.

There are a number of possible explanations for why the volcanic ash additions stimulated phytoplankton more than Fe-only additions. A difference in total Fe supply between treatments appears to be unlikely for several reasons: (i) While some of the ash loadings were potentially capable of releasing more Fe than the 2 nmol L^{-1} Fe-spike (Figure S1 in the supporting information), this level would typically already be expected to be capable of relieving phytoplankton Fe stress. Overall biological demand for Fe might be expected to be relatively lower in the Drake Passage, where the lowest phytoplankton concentrations were observed. Drake Passage sites nonetheless responded to ash addition but not to the Fe-only spike, while other sites responded significantly to the same Fe-only amendment. (ii) Comparing the results of the laboratory ash leaching experiments for the two ash types suggested that the rhyolitic ash likely released significantly less Fe than the artificial Fe spike (see Text S1, Table S3, and Figure S1 in the supporting information). (iii) Despite differential Fe release per unit mass of ash (around 100% for a given ash type in leaching experiments, likely due to a heterogeneous distribution of soluble trace metals in/on the ash; see Table S3 in the supporting information), alongside significant variability in total loadings (Figure S1), similar phytoplankton responses were observed across bottles. For example, within experiment 12 the mass of ash added to individual bottles varied by an order of magnitude, yet the relative standard deviation of responses between bottles was less than 20%. Overall, the total Fe added during amendment (ash or spike) thus appeared to be an unlikely determining factor in phytoplankton responses.

Addition of acidified $FeCl_3$ will increase oxidized Fe (III) to concentrations which would promote rapid Fe precipitation unless immediately complexed by biologically produced organic ligands [*Schlosser et al.*, 2011]. In contrast, ash may release significant reduced Fe (II) (e.g., from $FeCl_2$ or FeF_2 salts) [*Duggen et al.*, 2010], which could persist in cold Southern Ocean waters for several hours prior to oxidation [*Croot and Laan*, 2002]. Furthermore, the dissolution or release kinetics of Fe from ash particles could result in a more continuous supply of Fe (II) for a limited period (~up to 1 h) [*Olgun et al.*, 2011]. As the Drake Passage waters were the coldest encountered (~2°C for surface waters) and might be expected to be characterized by low organic ligand concentrations due to low overall biomass [*Boye et al.*, 2001], semicontinuous Fe (II) delivery from ash resulting in a greater effective bioavailability to the resident phytoplankton population could be considered possible. However, the ubiquity of the enhanced ash response across >3 orders of magnitude in ash loading (Figure S1 in the supporting information) argues against such an explanation. We therefore consider (co) limitation of phytoplankton by another essential trace metal nutrient to be the most likely explanation for the marked enhancement in phytoplankton response to ash addition.

Colimitation of phytoplankton by Mn in Drake Passage was suggested as early as 1990 by Martin and coworkers [*Martin et al.*, 1990], although no subsequent direct evidence has been found. Our Mn data demonstrated surface concentrations in this region to be amongst the lowest ever measured in seawater (Figure 2c) [*Middag et al.*, 2011, 2012, 2013], with dissolved Mn:Fe ratios as low as 0.16 being well below typical phytoplankton cellular Mn:Fe ratios [*Moore et al.*, 2013]. Mn is required for a variety of biological processes, including as an essential and nonsubstitutable cofactor in the oxygen-evolving complex of photosystem II within the light reactions of photosynthesis [*Morel et al.*, 2003]. Moreover, Mn requirements and Mn:Fe ratios may be particularly enhanced under Fe limitation [*Middag et al.*, 2013; *Peers and Price*, 2004], with relief of Fe-Mn colimitation resulting in enhanced growth and F_v/F_m in laboratory phytoplankton cultures [*Peers and Price*, 2004]. The basaltic ash released far more Fe than the rhyolitic ash, while, in contrast, both ashes released similar amounts of Mn (Table S3 in the supporting information). Consequently, we suggest that the observed similarity in enhanced phytoplankton responses to both ash types indicates the potential significance of relief of Mn (co)limitation.

The clear phytoplankton responses we observed to ash addition have important implications for Southern Ocean biogeochemistry. Enhanced phytoplankton growth following ash addition would be expected to increase the flux of CO_2 between the atmosphere and the surface ocean organic carbon pool, and potentially drive a shift to larger, more rapidly sinking taxa [*Boyd et al.*, 2007; *Smetacek et al.*, 2012; *Moore et al.*, 2007] enhancing carbon export to the deep ocean where it can remain sequestered for centuries or longer [*Sigman et al.*, 2010; *Williams and Follows*, 2011]. In comparison to the recent European Iron Fertilization Experiment (EIFEX), where a few thousand tons of carbon was estimated to be sequestered from a fertilization area of only 167 km^2 [*Smetacek et al.*, 2012], the much larger aereal extent (Figure 1) and enhanced stimulatory response (Figures 2d–2f and 3) which would likely accompany a major ash deposition event could thus potentially result in regionally or even globally significant carbon sequestration [*Watson*, 1997].

Although requiring further verification, both our suggested explanations for the significantly enhanced stimulatory response to ash over that of Fe alone (namely greater bioavailability of ash-released Fe (II) and/or the release of (co)limiting Mn) would also have important biogeochemical implications. Specifically, we suggest that significant changes in the biogeochemistry of Drake Passage, which currently represents some of the lowest-chlorophyll high-nitrate waters found anywhere in the surface ocean, may not simply depend on overall increases in Fe supply. Rather, the form of external Fe delivery may be significant and/or an accompanying Mn input might be required to drive significantly enhanced productivity and carbon export. Thus, for example, as sedimentary Fe sources might be expected to be accompanied by Mn [e.g., *Measures et al*., 2013; *Hatta et al*., 2013], the combined input of both Fe and Mn may be partially responsible for near coastal phytoplankton responses observed in Drake Passage [e.g., *Hopkinson et al*., 2007].

Irrespective of the exact cause for our observations, erupted volcanic material appears to be an effective fertilizer for this region. The Drake Passage and the western margin of the South Atlantic are areas of the Southern Ocean that are highly prone to tephra deposition from explosive volcanic eruptions [*Olgun et al*., 2011; *Fontijn et al*., 2014]. Large late Quaternary eruptions from volcanoes of both the Andean Austral and Southern Volcanic Zones have deposited considerable volumes of andesitic to rhyolitic tephra across the Drake Passage and into Antarctica [*Stern*, 2008; *Narcisi et al*., 2012]; while several eruptions per century from Patagonian volcanoes have delivered tephra to the western reaches of the South Atlantic [*Scasso et al*., 1994]. Rates and sizes of eruptions may well have varied significantly between peak-glacial and postglacial times, depending on the extent of ice cover across Patagonia [*Watt et al*., 2013]. Consequently, there is the potential for long time scale variability in the extent of ash-driven fertilization and carbon export from these waters.

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