Natural iron fertilization by the Eyjafjallajökull volcanic eruption

Eric P. Achterberg, ¹ C. Mark Moore, ¹ Stephanie A. Henson, ¹ Sebastian Steigenberger, ¹ Andreas Stohl, ² Sabine Eckhardt, ² Lizeth C. Avendano, ¹ Michael Cassidy, ¹ Debbie Hembury, ¹ Jessica K. Klar, ¹ Michael I. Lucas, ³ Anna I. Macey, ¹ Chris M. Marsay, ¹ and Thomas J. Ryan-Keogh ¹

Received 19 November 2012; revised 27 January 2013; accepted 3 February 2013; published 14 March 2013.

[1] Aerosol deposition from the 2010 eruption of the Icelandic volcano Eyjafjallajökull resulted in significant dissolved iron (DFe) inputs to the Iceland Basin of the North Atlantic. Unique ship-board measurements indicated strongly enhanced DFe concentrations (up to 10 nM) immediately under the ash plume. Bioassay experiments performed with ash collected at sea under the plume also demonstrated the potential for associated Fe release to stimulate phytoplankton growth and nutrient drawdown. Combining Fe dissolution measurements with modeled ash deposition suggested that the eruption had the potential to increase DFe by $>0.2 \,\mathrm{nM}$ over an area of up to 570,000 km². Although satellite ocean color data only indicated minor increases in phytoplankton abundance over a relatively constrained area, comparison of in situ nitrate concentrations with historical records suggested that ash deposition may have resulted in enhanced major nutrient drawdown. Our observations thus suggest that the 2010 Eyjafjallajökull eruption resulted in a significant perturbation to the biogeochemistry of the Iceland Basin. Citation: Achterberg, E. P., C. Mark Moore, S. A. Henson, S. Steigenberger, A. Stohl, S. Eckhardt, L. C. Avendano, M. Cassidy, D. Hembury, J. K. Klar, M. I. Lucas, A. I. Macey, C. M. Marsay, and T. J. Ryan-Keogh (2013), Natural iron fertilization by the Eyjafjallajökull volcanic eruption, Geophys. Res. Lett., 40, 921–926, doi:10.1002/grl.50221.

1. Introduction

[2] The trace nutrient Fe limits phytoplankton growth in approximately 30% of the world's oceans [Boyd and Ellwood, 2010] (the so-called high-nitrate low-chlorophyll (HNLC) regions). Inputs of Fe from aeolian mineral dust are important in remote ocean regions, and their effects on primary productivity and nitrogen fixation have received considerable attention [Jickells et al., 2005; Moore et al., 2009]. Volcanic ash emissions and subsequent aerosol deposition to the surface ocean have also frequently been implicated as a source of Fe [Duggen et al., 2010; Frogner et al., 2001; Sarmiento, 1993;

Corresponding author: E.P. Achterberg, National Oceanography Centre Southampton, University of Southampton, European Way, Southampton, SO14 3ZH, UK. (eric@noc.soton.ac.uk)

©2013. American Geophysical Union. All Rights Reserved. 0094-8276/13/10.1002/grl.50221

Watson, 1997]. Increased productivity in both the modern [Langmann et al., 2010] and paleo oceans [Cather et al., 2009] has been linked to volcanism; however, direct observations of ash deposition and biogeochemical responses are scarce due to the intermittent and unpredictable nature of events. Nevertheless, observed decreases in atmospheric CO₂ following the large eruptions of Agung (1963) and Pinatubo (1991) have been interpreted in terms of the fertilizing effects of ash-derived Fe on ocean productivity [Cather et al., 2009; Sarmiento, 1993; Watson, 1997]. More recently, ocean color satellite observations provided evidence for enhanced phytoplankton growth in the HNLC Northeast Pacific following the eruption of the Kasatochi Volcano in 2008 [Hamme et al., 2010; Langmann et al., 2010] and in the low-nutrient low-chlorophyll North Pacific following the Anatahan eruption in 2003 [Lin et al., 2011].

[3] The explosive eruption of the Eyjafjallajökull Volcano commenced on 14 April 2010, following two decades of intermittent seismic unrest [Dahm and Brandsdóttir, 1997]. Highly variable ash particle (tephra) emissions continued until 22 May, discharging $\sim 270 \pm 70 \cdot 10^6 \,\mathrm{m}^3$ into the atmosphere to a height of up to 10 km [Gudmundsson et al., 2012]. Due to interactions with the glacier of the ice-capped volcano [Sigmundsson et al., 2010], a large fraction of the emitted ash was sufficiently fine grained for long-range transport [Stohl et al., 2011]. An estimated 75% of the emitted particle mass with a size fraction of 0.25-250 µm was deposited in the ocean [Stohl et al., 2011]. We investigated the effects of the tephra-associated Fe inputs on the biogeochemistry of the Iceland Basin of the North Atlantic. Following a pronounced annual spring bloom, this region typically features residual nitrate (2-5 µM) and low dissolved iron (DFe; 0.01-0.2 nM) and chlorophyll (Chl; $0.2-0.4 \,\mu\text{g}\,\text{l}^{-1}$) concentrations in surface waters in summer [Nielsdóttir et al., 2009; Ryan-Keogh et al., 2013; Sanders et al., 2005], and thus, increased Fe supply can potentially enhance the efficiency of the biological carbon pump.

2. Material and Methods

[4] Observations were undertaken in the North Atlantic during three cruises in 2010 (Spring: 26 April to 9 May and 10–28 May; Summer: 4 July to 11 August). Full details of all materials and methods are provided in the Supporting Information, and here we provide a brief outline. Seawater was pumped from a depth of approximately 3 m using trace metal clean techniques and sampled every 2 h. Dissolved Fe and aluminum (Al) (0.2 µm filtered) were analyzed using flow injection techniques [*Brown and Bruland*, 2008; *Obata et al.*, 1993], Fe ligands using electrochemistry [*Croot and*

All Supporting Information may be found in the online version of this article.

¹National Oceanography Centre Southampton, University of Southampton, Southampton, UK.

²Norwegian Institute for Air Research, Kjeller, Norway.

³Marine Research Institute, University of Cape Town, Rondebosch, South Africa.

Johansson, 2000], nutrients using an auto-analyzer [Grasshoff et al., 1983], and Chl a using a fluorescence method [Welschmeyer, 1994].

[5] Aerosols were collected using low-volume collectors and subjected to a rapid de-ionized water leach [Buck et al., 2006] and a hydrofluoric acid (HF) digest [Ottley et al., 2003] followed by inductively coupled plasma-mass spectrometry (ICP-MS) analysis. Volcanic ash collected under the plume was analyzed with X-ray fluorescence, and ICP-MS after HF digestion. Bioassay experiments were conducted on the summer cruise using established trace metal clean protocols [Moore et al., 2006]. Seawater was collected using the towed fish, and incubations were performed in parallel as triplicate controls and following the addition of 2 nM FeCl₃ and 9 mg l⁻¹ of the ash collected under the plume (8 May), both alone and in combination. Biological variables including Chl and apparent photochemical quantum efficiencies as derived by fast repetition rate fluorometry (FRRf) were measured in situ and within experiments [Rvan-Keogh et al., 2013]. MODIS satellite observations for Chl, aerosol optical thickness, and fluorescence line height data were obtained from NASA.

[6] Dispersion and deposition of volcanic ash emissions were calculated with a Lagrangian particle dispersion model using meteorological analysis data and a volcanic ash source term derived by inverse modeling of satellite observations [Stohl et al., 2011].

3. Results and Discussion

[7] Serendipitously, the RRS *Discovery* was undertaking three cruises within the Iceland Basin and wider highlatitude North Atlantic both during (spring cruises) and following (summer cruise) the explosive eruption phase of the Eyjafjallajökull Volcano. Consequently, on 8 May we

had the unique opportunity to sample directly underneath the eruptive plume (Figure 1), which was rotating in a clockwise direction at the time (Figure S1). Water samples with relatively low DFe (0.23–0.45 nM) collected directly prior to encountering the plume were thus in a region which had not recently been exposed to deposition. Ash inputs to the sampled region had been low immediately prior to 5 May but increased to a peak on 8 May (Figure S2) [Stohl et al., 2011] when we encountered high deposition immediately under the plume. Atmospheric ash concentrations were ~6 mg m⁻³ within the plume, with an ash layer of a few millimeters thick accumulating on the ship's deck within 30 min.

[8] Highly elevated concentrations of DFe (maximum 10.2 nM) and DAI (maximum 45 nM; DAI is a tracer for aerosol inputs [Measures and Vink, 2000]) (Figure 1) were observed directly under the plume (63.1°N, 18.5°W), in contrast to more typical concentrations in Icelandic coastal surface waters of approximately 0.2-0.6 nM DFe and approximately 2-3 nM DAI (63°N, 19-20°W; July-August 2010 cruise). Moreover, a station occupied on 12 May at 63.3°N, 20.1°W (70–80 km west of the 8 May sampling location) also indicated enhanced DFe in the surface mixed layer (1.39–2.05 nM), compared to a previous observation of 0.56-0.90 nM at the same location in June 2009. Movement of the ash plume (Figure S1), combined with the likely timescales of any biological responses [Nielsdóttir et al., 2009] (also Figure 2), restricted the inferences which could be drawn from biological sampling directly beneath the plume. However, FRRf measurements [Suggett et al., 2009] indicated high photosynthetic efficiencies (>0.55) within the natural phytoplankton populations sampled directly under the plume, suggesting that acute local trace metal toxicity [Duggen et al., 2010; Hoffmann et al., 2012] was unlikely.

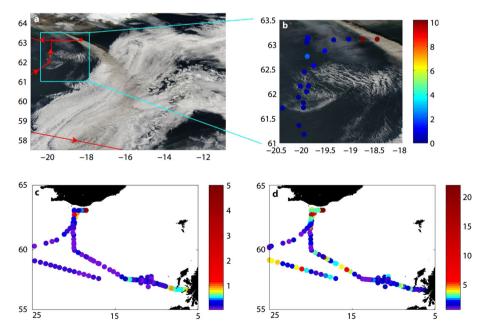


Figure 1. (a) Satellite image of volcanic ash plume for 8 May 2010, with ship track superimposed. The sampling station for 8 May is indicated as a red circle. (b) Enlarged image of the region in vicinity of the ash plume (13:35 UTC on 8 May), with DFe (in nM) in surface waters as determined in situ during 6–8 May and 12–14 May. Two samples with highly enhanced DFe (>10nM) were sampled directly under plume at ~15:02 and 15:59 UTC on 8 May. (c, d) DFe and DAI (in nM) in surface waters of the North Atlantic as determined in situ during 28 April to 23 May.

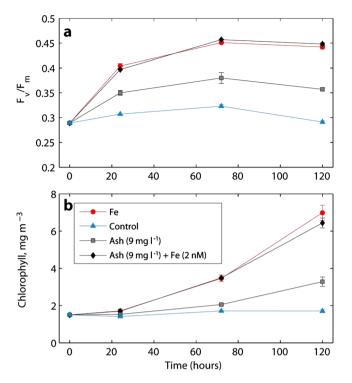


Figure 2. Response of bulk phytoplankton community to Fe and ash additions in an experiment performed at 63.8° N -34.7° W, showing results for controls, additions of 2 nM dissolved FeCl₃, additions of 9 mg l⁻¹ volcanic ash, and additions of 9 mg l⁻¹ volcanic ash + 2 nM FeCl₃. (a) Phytoplankton photochemical efficiency F_v/F_m against time. (b) Chl concentration against time. Shown are mean values (± 1 standard error, n=3).

[9] Stimulation of phytoplankton productivity by ash deposition requires the addition of a previously limiting nutrient. The high-latitude North Atlantic, where Fe availability is clearly sufficient to sustain a highly productive spring bloom, is not a classical HNLC region [Martin et al., 1993]. However, there is evidence for the development of Fe stress within phytoplankton communities in the region as the bloom progresses toward the peak and postbloom stages [Nielsdóttir et al., 2009; Ryan-Keogh et al., 2013]. In order to establish whether ash deposition had the potential to generate a significant biological effect, we experimentally added ash collected under the plume to natural phytoplankton populations during our summer cruise in 2010 (Figure 2). Experiments performed in the Irmminger Basin region, which received much lower ash deposition (Figure 3), and where observed residual surface major nutrients in summer were high (nitrate $5.2 \pm 0.2 \,\mu\text{M}$) and DFe was relatively low (0.037-0.051 nM) indicated clear evidence of Fe stress [Ryan-Keogh et al., 2013] alongside a significant response of phytoplankton to the 9 mg l⁻¹ ash addition (Figure 2). Addition of ash combined with Fe further confirmed the absence of acute toxic effects, at least for the extant phytoplankton population (Figure 2).

[10] Although ash addition clearly promoted a rapid (\sim 24 h) photo-physiological response and subsequently stimulated net Chl accumulation and nutrient drawdown within our experiments (Figures 2 and S3), the magnitude of these effects was modest. Addition of 9 mg l⁻¹ of ash had less than half the

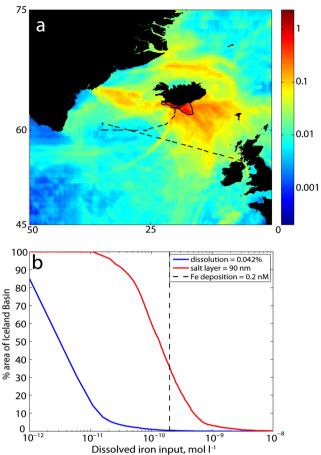


Figure 3. (a) Modeled DFe enhancement (nM) as a result of ash deposition (15 April to 23 May) using midrange estimates of salt layer thickness (20 nm) of volcanic particles as obtained through leaching experiments. Contours mark 0.2 nM DFe enhancement. The dashed line is the cruise track (May 2010). (b) The proportion of the Iceland Basin (assumed to be a region $\sim 1 \times 10^6 \, \mathrm{km}^2$) receiving DFe inputs from ash (15 April to 23 May) using minimum (solubility 0.042%) and maximum (salt layer coating of 90 nm thickness) estimates of Fe content of volcanic particles.

stimulatory influence of a 2 nM DFe addition. Chemical analysis of the ash collected at sea indicated 7.59% Fe by weight (Table S1), consistent with other reports (e.g., 7.75% [Gislason et al., 2011]). Hence, only a small fraction of our total particulate Fe (PFe) addition of $\sim\!12\,\mu\text{M}$ appeared to become available to the natural biota within our experiments. Indeed the magnitude of observed biological responses suggested that at most 0.02% of the total Fe became bioavailable.

[11] In contrast, results from a rapid leach [Buck et al., 2006] conducted with the ash collected at sea on 8 May, yielded 511–1740 nmol DFe g⁻¹ ash and hence an Fe solubility of 0.042% to 0.143% in de-ionized water. These values represent instantaneous Fe solubility upon ash entering the ocean [Buck et al., 2006] and are comparable to, although slightly higher than, the range of 100–400 nmol g⁻¹ ash reported for subduction zone volcanoes [Duggen et al., 2010]. Dissolved Fe inputs are likely dominated by the highly soluble salt layer of metal sulphates and halides formed on ash particles within volcanic plumes through

reactions with acidic gases (i.e., HF, HCl, and SO_2) and aerosols (i.e., H_2SO_4) [Duggen et al., 2010]. Direct estimates of salt layer thickness on particles collected from the same eruption of Eyjafjallajökull yielded values of up to 300 nm, while an average thickness of 7 nm contributed approximately 0.6% of the ash particle weight with an Fe content of 3.1% [Gislason et al., 2011]. Combining our observed ash size spectrum (peaking at 123 μ m, Figure S4), with a conservative range of 3–7.5% Fe content, we similarly estimate that complete dissolution of an average salt layer of ~20–90 nm would have been consistent with our leaching results for the ash we collected at sea.

[12] Although solubility in seawater may have been lower than that in de-ionized water [Buck et al., 2006], leaching data thus indicated that addition of 9 mg l⁻¹ ash within biological incubation experiments could have provided 4.6–16 nM DFe. In contrast, observed biological responses were weaker than for the 2 nM FeCl₃ addition. Hence, in addition to much of the PFe addition being nonbioavailable, a significant fraction of the DFe released from ash particles may also not become available to the extant phytoplankton community, at least over the timescales of our experiments, which were likely comparable to residence times for ash in the upper ocean (see Supporting Information specifically Figure S5). The observed surface water concentrations of Febinding ligands (L) in excess of DFe (L' = L - DFe) ranged between 0.33 and 1.77 nM during the summer cruise for the Iceland Basin region affected by ash inputs (Figure S1), compared to 0.37-0.94 nM during cruises in the Iceland Basin in 2007 and 2009 [Mohamed et al., 2011]. Concentrations of L' similarly ranged between 0.16 and 1.22 nM for the region of the North Atlantic where the bioassay experiments were undertaken during the summer cruise. These observations suggest that cumulative DFe inputs exceeding ~1–2 nM cannot be stabilized by the available free ligand L' in seawater and hence may be lost through rapid precipitation both within our experiments and in situ.

[13] We estimate the contribution of the Eyjafjallajökull ash to DFe inputs to the region using an atmospheric particle dispersion model [Stohl et al., 2005, 2011] constrained with satellite observations of volcanic ash (Figure 3). For simplicity, we initially assume that all modeled size classes (25, from 0.25 to 250 µm) had the same chemical composition and dissolution characteristics as our samples collected at sea. Resulting best estimates (and upper bounds) for the DFe input to the North Atlantic over the course of the eruption were ~550 kmoles (1800 kmoles), assuming 0.042-0.143% Fe dissolution, with DFe increases >1 nM only occurring in the immediate vicinity of the volcano, while a region of ~10,000 km² (42,000 km²) was predicted to have accumulated >0.2 nM DFe. If, in contrast, we assume that all size classes were coated with a highly soluble salt layer ranging from 7 to 90 nm thick, then a region of $26,000-570,000 \,\mathrm{km}^2$ could have accumulated $> 0.2 \,\mathrm{nM}$ DFe. Such sensitivity analyses emphasize that estimates of DFe inputs (Figures 3b and S6) from volcanic eruptions remain highly sensitive to poorly constrained assumptions regarding

[14] Satellite ocean color data has previously been used to infer basin-scale responses to ash inputs in the HNLC North Pacific. For the region of the Iceland Basin where potential DFe enhancement was >0.2 nM (assuming a salt layer thickness of 20 nm), the typical annual phytoplankton bloom

starts in early April and peaks in late June (Figure 4a). In contrast, during 2010 the time series of satellite-derived Chl indicated an early peak from early April through to late May in this region (Figure 4a). The phytoplankton bloom thus peaked anomalously early before returning to mean summer levels, suggestive of a rapid phytoplankton response to ash deposition in the northern Iceland Basin (Figure 4a). Satellite-derived fluorescence line height data displayed a similar signal (see the Supporting Information and Figure S7). These data provide a measure of the reflectance at a similar wavelength to Chl fluorescence and hence might be expected to be less sensitive to any problems with atmospheric corrections during the eruptive phase. The good agreement between the in situ Chl a data and the satellitederived Chl a data (no observable systematic differences) further supported the inference that the altered seasonal cycle observed within the satellite record was robust.

[15] Following the eruption, we observed near-complete nitrate depletion in the central Iceland Basin (59–61°N, 19–21°W) during summer, in contrast to previous years [Nielsdóttir et al., 2009] (Figure 4b). Consequently, we propose the following scenario. During typical years, this region of the Iceland Basin appears to be deficient in Fe, contributing to a residual major nutrient pool in summer [Nielsdóttir et al., 2009]. Enhanced Fe inputs as a result of the 2010 Eyjafjallajökull eruption and ash deposition may thus have increased phytoplankton growth rates within the early spring bloom [Moore et al., 2006], driving more complete depletion of the surface major nutrient pool, although the dynamics of this would clearly depend on both growth

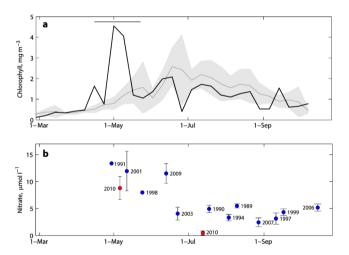


Figure 4. (a) Time series of satellite-derived Chl concentration averaged over regions where potential DFe enhancement was $>0.2\,\mathrm{nM}$ (assuming a salt layer thickness of 20 nm). The thick black line is the 2010 Chl; the thin grey line is the 2003–2009 mean Chl; the grey shading is the standard error of the 2003–2009 Chl. The black horizontal line marks the period of volcanic eruption. (b) Measured surface nitrate in the region between 60– $62^{\circ}\mathrm{N}$ and 19– $21^{\circ}\mathrm{W}$ from cruises between 26 April to 9 May and 4 July to 11 August, and historical data from the World Ocean Database [*Boyer et al.*, 2006] for the same region. Shown are the mean and standard deviation of nitrate against mean time of the year of observations during each cruise, individual years are labelled. Bars mark ± 1 standard deviation. Summer concentrations from 2010 are significantly lower than all other summer observations.

and loss terms, including grazing [Banse, 2002]. Irrespectively, the observed depletion of nitrate during summer 2010 would be expected to place a constraint on further increases in phytoplankton standing stocks, reducing the subsequent sensitivity to Fe inputs. Indeed, by summer, phytoplankton populations in the Iceland Basin displayed evidence of colimitation by nitrate and Fe [Ryan-Keogh et al., 2013]. Our proposed scenario is consistent with the early onset of the bloom (Figure 4a) and satellite-derived Chl concentrations following the peak bloom being below the mean after mid-June in regions proximal to the volcano.

[16] We clearly cannot exclude other causes of interannual variability as drivers of the observed anomalous time series of satellite-derived Chl and depletion of surface nitrate concentrations in the central Iceland Basin during 2010. If, as we suggest [Rvan-Keogh et al., 2013], Fe availability in the Iceland Basin is only just deficient of the level required for the annual new production to fully remove the end of winter surface nitrate pool (approximately 12-14 µM [Sanders et al., 2005]), any change in either Fe or nitrate inputs (or specifically the overall Fe:N input ratio) could influence whether nitrate becomes fully depleted in summer (Figure 4b). Our direct evidence of enhanced Fe (Figure 1) combined with estimated DFe inputs (Figure 3) and the experimentally established fertilization effect of ash-derived Fe (Figure 2) is at least suggestive of the viability of ash inputs as a mechanism for the observed nitrate depletion. However, even in a typical year, residual surface nitrate pools in summer (2-4 µM) are only around 10-20% of winter concentrations (Figure 4b). Consequently, the highlatitude North Atlantic is already characterized by highly efficient (>80%) major nutrient removal with only a restricted potential for any enhancement by Fe addition.

[17] Although the 5 week long eruption resulted in enhanced Fe inputs over a large area, during our post-eruption cruise in July–August, we found no evidence for elevated surface DFe in offshore waters of the Iceland Basin $(0.20\pm0.07\,\mathrm{nM}$ in 2010 compared with $0.18\pm0.17\,\mathrm{nM}$ in June 2009). This is consistent with the reported 2–7 week residence times for DFe in surface waters receiving enhanced atmospheric inputs [Sarthou et al., 2003]. The effects of this brief midsized eruption (estimated tephra emission $\sim 0.38\,10^9\,\mathrm{tonne}$; [Gudmundsson et al., 2012]) on the biogeochemical Fe cycle were therefore relatively short-lived. Interestingly, the bloom induced by the similarly sized Kasatochi eruption (estimated tephra emission of 0.65 $10^9\,\mathrm{tonne}$ over 2 days) within the HNLC North Pacific lasted for only 2 weeks [Hamme et al., 2010].

[18] Our study demonstrates that the Eyjafjallajökull eruption caused significant local impacts on oceanic Fe cycling (Figure 1). However, subsequent regional-scale biogeochemical effects on the high-latitude North Atlantic were modest at most, with enhanced nutrient drawdown (Figure 4b) indicating a maximal 10–20% increase in annual new production. The impact of the biological pump on the carbon cycle, and hence atmospheric CO₂, scales with surface major nutrient drawdown [Sigman and Boyle, 2000]. Therefore, the typical magnitude of the residual nitrate pool in the region sets an upper bound on any increase in integrated export production of ~5 g C m⁻² compared with an annual flux of ~30 g C m⁻² y⁻¹ [Sanders et al., 2005].

[19] In order for Fe supply from volcanic eruptions to have a larger-scale influence on atmospheric CO₂ drawdown, as

previously suggested [Sarmiento, 1993], ash emissions would therefore likely have to be much larger than the Eyjafjallajökull event, with sustained deposition spread over an extensive HNLC region where removal of a larger residual major nutrient pool can occur due to a lower preexisting biological pump efficiency.

[20] **Acknowledgments.** We thank all the scientists and crew on D350 and D354 (RRS *Discovery*). We acknowledge Drs. T. Bibby, A. Poulton, C. Thompson, and S. Painter for the discussion of results. MODIS data were provided by GSFC/NASA. This work was funded by NERC (NE/E006833/1, EPA & CMM; NE/G013055/1, SAH).

References

Banse, K. (2002), Steemann Nielsen and the zooplankton, Hydrobiologia, 480(1-3), 15-28.

Boyd, P. W., and M. J. Ellwood (2010), The biogeochemical cycle of iron in the ocean, *Nature Geoscience*, 3(10), 675–682.

Boyer, T. P., et al. (2006), Introduction, NOAA Atlas NESDIS 60, in World Ocean Database 2005, edited by S. Levitus, p. 182, U.S. Government Printing Office, Washington.

Brown, M. T., and K. W. Bruland (2008), An improved flow-injection analysis method for the determination of dissolved aluminum in seawater, *Limnol. Oceanogr. Methods.* 6, 87–95.

Buck, C. S., et al. (2006), Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise, *Geochem. Geophys. Geosyst.*, 7.

Cather, S. M., et al. (2009), Climate forcing by iron fertilization from repeated ignimbrite eruptions: The icehouse-silicic large igneous province (SLIP) hypothesis, *Geosphere*, 5(3), 315–324.

Croot, P. L., and M. Johansson (2000), Determination of iron speciation by cathodic stripping voltammetry in seawater using competing ligand 2-(2thiazolylazo)-p-cresol (TAC), *Electroanalysis*, 12, 565–576.

Dahm, T., and B. Brandsdóttir (1997), Moment tensors of microearthquakes from the Eyjafjallajökull volcano in South Iceland, *Geophys. J. Int.*, 130(1), 183–192.

Duggen, S., et al. (2010), The role of airborne volcanic ash for the surface ocean biogeochemical iron-cycle: A review, *Biogeosciences*, 7(3), 827–844.
 Frogner, P., et al. (2001), Fertilizing potential of volcanic ash in ocean

surface water, Geology, 29(6), 487–490.

Gislason, S. R., et al. (2011), Characterization of Eyjafjallajokull volcanic ash particles and a protocol for rapid risk assessment, *Proc. Nat. Acad.* Sci., 108, 7307–7312.

Grasshoff, K., et al. (1983), Methods of Seawater Analysis, Verlag Chemie, Weinheim.

Gudmundsson, M. T., et al. (2012), Ash generation and distribution from the April-May 2010 eruption of Eyjafjallajokull, Iceland, *Nature Scientific Re*ports, 2, doi:10.1038/srep00572.

Hamme, R. C., et al. (2010), Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific, *Geophys. Res. Lett.*, *37*(19), L19604.

Hoffmann, L. J., et al. (2012), Influence of trace metal release from volcanic ash on growth of *Thalassiosira pseudonana* and *Emiliania huxleyi*, *Marine Chemistry*, 132–133(0), 28–33.

Jickells, T. D., et al. (2005), Global iron connections between desert dust, ocean biogeochemistry, and climate, *Science*, 308(5718), 67–71.

Langmann, B., et al. (2010), Volcanic ash as fertiliser for the surface ocean, *Atmos. Chem. Phys.*, 10(8), 3891–3899.

Lin, I. I., et al. (2011), Fertilization potential of volcanic dust in the low-nutrient low-chlorophyll western North Pacific subtropical gyre: Satellite evidence and laboratory study, *Global Biogeochem. Cycles*, 25(1), GB1006.

Martin, J. H., et al. (1993), Iron, primary production and carbon-nitrogen flux studies during the JGOFS North Atlantic Bloom Experiment, *Deep-Sea Research II*, 40, 115–134.

Measures, C. I., and S. Vink (2000), On the use of dissolved aluminium in surface waters to estimate dust deposition to the ocean, *Global Biogeochem. Cycles*, 14(1), 317–327.

Mohamed, K. N., et al. (2011), Dissolved iron(III) speciation in the high latitude North Atlantic Ocean, *Deep-Sea Res. I*, 58(11), 1049–1059.

Moore, C. M., et al. (2006), Iron limits primary productivity during spring bloom development in the central North Atlantic, *Glob. Change. Biol.*, 12(4), 626–634.

Moore, C. M., et al. (2009), Large-Scale distribution of Atlantic nitrogen fixation controlled by iron availability, *Nat. Geosci.*, 2(12), 867–871.

Nielsdóttir, M. C., et al. (2009), Iron limitation of the postbloom phytoplankton communities in the Iceland Basin, *Global Biogeochem. Cycles*, 23(3), GB3001.

ACHTERBERG ET AL.: IRON FERTILIZATION BY VOLCANIC ERUPTION

- Obata, H., et al. (1993), Automated determination of iron in seawater by chelating resin concentration and chemiluminescence detection, *Anal. Chem.*, 65, 1524–1528.
- Chem., 65, 1524–1528.

 Ottley, C. J., et al. (2003), A routine method for the dissolution of geological samples for the analysis of REE and trace elements via ICP-MS, in *Plasma Source Mass Spectrometry: Applications and Emerging Technologies*, edited by J. G. Holland and S. D. Tanner, pp. 221–230, Royal Society of Chemistry, Cambridge.
- Ryan-Keogh, T. J., et al. (2013), Spatial and temporal development of phytoplankton iron stress in relation to bloom dynamics in the high-latitude North Atlantic Ocean, *Limnol. and Oceanogr.*, 58(2), 533–545.
- Sanders, R., et al. (2005), New production in the Irminger Basin during 2002, *J. Marine. Syst.*, 55(3–4), 291–310.
- Sarmiento, J. L. (1993), Atmospheric CO2 stalled, *Nature*, *365*, 697–698. Sarthou, G., et al. (2003), Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean, *Deep-Sea Res. I*, *50*(10–11), 1339–1352.

- Sigman, D. M., and E. A. Boyle (2000), Glacial/interglacial variations in atmospheric carbon dioxide, *Nature*, 407(6806), 859–869.
- Sigmundsson, F., et al. (2010), Intrusion triggering of the 2010 Eyjafjallajokull explosive eruption, *Nature*, 468(7322), 426–430.
- Stohl, A., et al. (2005), Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, Atmos. Chem. Phys., 5(9), 2461–2474.
- Stohl, A., et al. (2011), Determination of time- and height-resolved volcanic ash emissions and their use for quantitative ash dispersion modeling: The 2010 Eyjafjallajokull eruption, Atmos. Chem. Phys., 11(9), 4333–4351.
- Suggett, D., et al. (2009), Interpretation of fast repetition rate (FRR) fluorescence: signatures of phytoplankton community structure versus physiological state, *Mar. Ecol.-Prog. Ser.*, 376, 1–19.
- Watson, A. J. (1997), Volcanic iron, CO₂, ocean productivity and climate, *Nature*, 385(6617), 587–588.
- Welschmeyer, N. A. (1994), Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and pheopigments, *Limnol. and Oceanogr.*, 39(8), 1985–1992.