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Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: Evidence from biogeochemical experiments and satellite data

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[1] Volcanoes confront Earth scientists with new fundamental questions: Can airborne volcanic ash release nutrients on contact with seawater, thereby excite the marine primary productivity (MPP); and, most notably, can volcanoes through oceanic fertilization affect the global climate in a way that is so far poorly understood? Here we present results from biogeochemical experiments showing that 1) volcanic ash from subduction zone volcanoes rapidly release an array of nutrients (co-)limiting algal growth in vast oceanic areas, 2) at a speed much faster (minute-scale) than hitherto known and that marine phytoplankton from low-iron oceanic areas can swiftly, within days, utilize iron from volcanic sources. We further present satellite data possibly indicating an increase of the MPP due to the seaward deposition of volcanic particulate matter. Our study supports the hypothesis that oceanic (iron) fertilization with volcanic ash may play a vital role for the development of the global climate. **Citation:** Duggen, S., P. Croot, U. Schacht, and L. Hoffmann (2007), Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: Evidence from biogeochemical experiments and satellite data, *Geophys. Res. Lett.*, *34*, L01612, doi:10.1029/2006GL027522.

1. Introduction

[2] The availability of nutrients in the surface ocean strongly affects the MPP and can therefore have a substantial influence on the development of the global climate [*Falkowski et al.*, 1998; *Morel and Price*, 2003]. Almost two decades ago it was discovered that iron limits phytoplankton growth in vast oceanic areas [*Martin and Fitzwater*, 1988]. Since then it was hypothesized that particulate matter from major volcanic eruptions (e.g. Pinatubo 1991, Philippines subduction zone) may release sufficient iron and other nutrients to the surface ocean to stimulate the MPP and trigger global atmospheric CO_2-drawdown [*Sarmiento*, 1993; *Watson*, 1997]. Moreover, oceanic fertilization with Fe from volcanic ash is thought to be partly responsible for a termination of global warmth at the Paleocene/Eocene boundary and for millennial climate change through MPP feedback [*Bains et al.*, 2000; *Bay et al.*, 2004].

[3] The rapid fertilizing potential of volcanic ash particles arises from a coating containing nutrient-bearing soluble salts formed from the gas phase during the eruption (e.g. condensed volcanic gases and adsorbed aerosols) [*Frogner et al.*, 2001]. A pioneer study with seawater and a single ash sample from the Icelandic Hekla volcano shows that ash from volcanoes in hot spot tectonic settings can release substantial amounts of macro- and micro-nutrients such as PO_4^{3-}, Si, Fe, Zn, Mn, Ni, Co and Cu within 1–2 hours [*Frogner et al.*, 2001]. However, volcanic gases from hot spot and subduction zone (SZ) volcanoes strongly differ in composition [*Oppenheimer*, 2004] and therefore volcanic ash coatings from these fundamentally different tectonic settings can be expected to have different nutrient contents and ratios underlining the necessity to examine the nutrient mobilization behaviour of subduction zone volcanic ash.

[4] This is particularly important for future quantitative assessments of the significance of volcanoes for oceanic fertilization, since most of the >5,300 historical subaerial volcanic eruptions occurred in subduction zones and due to their explosive nature SZ volcanoes are capable of transporting huge amounts of ash far into the ocean basins [*Sigurdsson et al.*, 2000], where trace metal levels usually are low. The majority of SZ volcanoes in turn are found in the Pacific Ring of Fire encircling the Pacific Ocean covering almost 50% of the Earth's oceanic surface and, notably, hosting the largest surface ocean area with very low-iron concentrations (Figure 1).

[5] Rapid stimulation of the MPP upon seaward volcanic ash deposition can only be expected at water depths where phytoplankton thrives, i.e. in the sunlit euphotic zone of the surface ocean (~100 m). Yet it remains unclear whether nutrients from SZVA particles, while sinking through the water column, are mobilized sufficiently swiftly, i.e. within the euphotic zone, or in the darkness of the sea. For the ocean-atmosphere interchange of CO_2 diatoms appear to take centre stage (e.g. due to the high C/Fe ratio of their tissue) [*Smetacek*, 2000; *Watson*, 1997] but, although generally expected, it is until now uncertain if marine diatoms can utilize volcanic iron for building up biomass, which may depend on the speciation of iron and the contemporaneous release of toxic metal ions. Together, short time-scale studies of the nutrient and toxic metal mobilization behaviour of SZVA and biogeochemical experiments are presently important for improving our understanding of the causal connection between volcanism, oceanic (iron) fertilization, enhancement of the MPP, the ocean-atmosphere interchange

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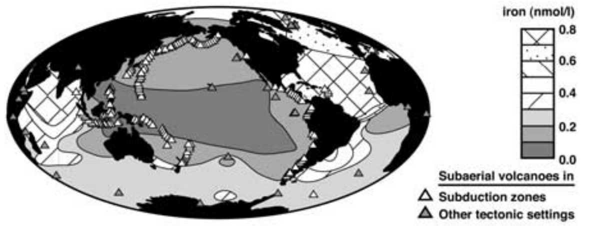

Figure 1. Map illustrating the surface ocean iron concentrations (modified from *Parekh et al.* [2005]) and distribution of subaerially active volcanoes [*Sigurdsson et al.*, 2000] on Earth. Subduction zone volcanoes are concentrated along the Pacific Ring of Fire encircling the largest ocean basin and the global minimum of surface ocean iron concentration.

of CO_2 and sulfur compounds, and ultimately global climate development.

2. Samples and Results

[6] The volcanic ash samples used for geochemical experiments in this study stem from subduction zone volcanoes located thousands of kilometers apart in the Pacific Ring of Fire: Arenal in Costa Rica, Sakura-jima in Japan and Mt. Spurr in Alaska (Figure 1). As airborne volcanic ash particles have soluble coatings containing nutrients [*Frogner et al.*, 2001] it is crucial to conduct oceanic fertilization studies with ash that has neither been in contact with rain- nor seawater following deposition (unhydrated ash). The release of 1) trace metals was determined *in situ* in low-metal Antarctic seawater by means of Anodic Stripping Voltammetry and 2) fixed N species, PO_4^{3-} and SiO_4^{4-} in the course of agitation experiments using low-nutrient Atlantic seawater. Details about analytical methods and data tables are found in the online auxiliary material[1].

[7] As illustrated in Figure 2a, on contact with ocean water, unhydrated SZVA swiftly release significant amounts of an array of important nutrients. Despite the wide distribution of their volcanic sources, the ash samples exhibit remarkably similar mobilization patterns with the highest mobilization rates within the initial 5–15 minutes and a fairly restricted variation of their nutrient release. Within 20 minutes each gram of ash liberated between 10–60 nmol of Fe, 2–27 nmol of Zn and 0–50 nmol of Cu (Figure 2a). Fe concentrations rose further within the first hour and thereafter even redoubled at 15 hours contact time as measured for the Arenal ash sample. The subsequent slight but steady decrease of the Zn and Cu concentrations following an initial pulse may be attributed to partial re-adsorption of Zn and Cu to ash particle surfaces. Only trace amounts of Cd and Pb, however, came off. Agitation experiments illustrate that SZVA instantly mobilize fixed N in significant amounts but, remarkably, primarily as NH_4^+ ($\sim$81–98% of the total N) rather than NO_3^- and NO_2^-, along with some PO_4^{3-} and Si (Figure 2a). Each gram of ash released between 200–1,100 nmol NH_4^+, 10–450 nmol NO_3^-, <50 nmol NO_2^-, 10–100 nmol PO_4^{3-} and 50–200 nmol Si. Trace metals are apparently released on a similar time scale as from Saharan aeolian dust [*Nimmo et al.*, 1998].

[8] In order to examine the possible biological effect of SZVA in iron-limited oceanic areas we performed bio-incubation experiments with the diatom *Chaetoceros dichaeta*, a common phytoplankton species in the Southern Ocean. We used Antarctic seawater doped with vitamins and nutrients (f/2 concentrations) except iron thereby creating an iron-limited system. For three of the six culture experiments the seawater was additionally in very brief contact (only 15–20 minutes!) with selected SZVA material having high initial mobilization rates for Fe as based on geochemical experiments (Figure 2a). As illustrated in Figures 3a and 3b, the phytoplankton in the bottles with SZVA-fertilized seawater show both a significant enhancement of the photosynthetic efficiency Fv/Fm and biomass (chlorophyll *a*) compared to the cultures that were grown without SZVA-fertilization. Within the first three days the SZVA-fertilized cultures exhibited a rapid increase of the photosynthetic efficiency that in the subsequent fourteen days stayed at a relatively high level ranging from 0.52 to 0.42 ± 0.03 (Figure 3a). This is significantly above the values observed for iron limited systems (<0.3, e.g. 0.20–0.25 in the Southern Ocean) [*Coale et al.*, 2004], whereas the cultures in the experiments without SZVA-fertilization swiftly fell back towards this level. After day six and until the termination of the experiment (after day 18) the increase of chlorophyll *a* in the SZVA-fertilized treatments was almost three times as high as for the populations grown under Fe-limited conditions (Figure 3b).

3. Discussion

[9] Our geochemical data for the first time provide a basis to explore the chemical impact of SZVA on surface ocean water. Based on Stokes' law and assuming deposition of individual grains, volcanic ash particles have euphotic zone residence times ranging from only a few minutes through 1–2 hours to 1–2 days for, resp., coarse (2,000–500 μm), intermediate (250–150 μm) and fine (<50 μm) ash particles. Aggregates of ash particles are frequently formed in the ash clouds of volcanic eruptions and are inferred to have high settling velocities in seawater (>1,670 meters/day) [*Wiesner et al.*, 1995], showing that even fine ash particles, as clusters, pass the euphotic zone swiftly within 1–2 hours.

[10] Since the mobilization rates are highest during the initial minutes (Figure 2a), the upper section (50 m) of the euphotic zone will be more prone to oceanic fertilization with SZVA: An ash layer of about 1 mm thickness distributed on a surface of 1 dm^2 (corresponding to $\sim$20 g of ash at 30% porosity) could raise the Fe concentration by about 0.4–2.4 nmol/l, Zn by 0.1–1.1 nmol/l, Cu by 0–2.0 nmol/l, total fixed N expressed as NO_3^- by 1–3.2 μmol/l (Figure 2a), PO_4^{3-} by 0.4–4.0 nmol/l and Si by 2.0–8.0 nmol/l (Figure 2b) (calculated for 50 m mixed layer depth). For an $\sim$1 cm ash layer these values would roughly be 10-fold and it is therefore important to emphasize that ash layers on the centi-, decimetre- and metre-scale were frequently found at numerous drill sites in the ocean basins [*Cao et al.*, 1995]. Notably, it was estimated that volcanic material makes up ca. 23% of the marine sediments in the Pacific about half of

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[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gl/2006GL027522. Other auxiliary material files are in the HTML.

which comes from subduction zones [*Straub and Schmincke*, 1998].

[11] SZVA would most likely have their largest impact on the ocean water chemistry where the concentrations of one or more nutrients are low. This is usually the case in the euphotic zone but becomes extreme in regions where the MPP is under-productive due to restricted nutrient availability (e.g. Fe) [*Martin and Fitzwater*, 1988]. In general these areas are the low- and high-nutrient- but low-productivity (LNLP and HNLP) areas in the Central Pacific, Central Atlantic, Central Indian and Southern Ocean (Figure 1) [*Chester*, 2000] that in terms of biologically important trace metal levels may be considered some of the most devilish habitats on Earth [*Morel and Price*, 2003]. In the surface ocean water of LNLP areas the nutrient concentrations are extraordinarily low (e.g. Fe and Zn <0.5 nmol/l, Cu <1 nmol/l and NO_3^- <~50 nmol/l) [*Bruland and Lohan*, 2004; *Dugdale and Wilkerson*, 1992] (Figures 1 and 2b). HNLP areas such as the Southern Ocean have excess NO_3^- (~20–30 μmol/l), variable Si ($\leq$5 μmol/l in low-Si- and $\geq$60 μmol/l in high-Si areas) but very low Fe contents (<0.5 nmol/l) [*Boyd et al.*, 2004; *Coale et al.*, 2004] (Figures 1 and 2b). Therefore, seaward deposition of even very thin layers of volcanic ash can significantly increase fixed N, Fe, Zn and Cu concentrations in LNLP areas and Fe, Zn and Cu in HNLP regions (Figure 2b). Consequently, SZVA can have an impact on the euphotic zone nutrient budget in as much as ~70% of the oceanic areas on Earth. However, drill core data for Pacific marine sediments suggest that most of the SZVA is deposited in the vicinity, i.e. <1,000 kilometers, of subduction zones, which in the Pacific Ocean is well within the low-productivity oceanic areas [*Straub and Schmincke*, 1998].

[12] Recent open ocean bioassay experiments show that oceanic fertilization is more effective when a combination of nutrients is added to surface ocean water rather than an individual growth-limiting element [*Mills et al.*, 2004]. This is associated with co-limitation of algal growth by additional nutrients that may play a crucial role for the acquisition and uptake of carbon, nitrogen, phosphorous and silica by marine phytoplankton (e.g. Fe, Zn and Cu in metalloenzymes and Si for silica shells in diatoms) and hence the build-up of biomass in the oceans. SZVA not only release the key trace metal Fe but also Zn, Cu, P, Si, and NH_4^+ (Figure 2) that is more readily incorporated into algae tissue than NO_3^-. Therefore, SZVA can be considered as a natural and rapidly working multi-fertilizer having the potential to excite the MPP in various oceanic areas.

[13] To our knowledge this study provides the first direct evidence that marine diatoms can utilize iron from volcanic sources. The swift coupled enhancements of Fv/Fm and Chl *a* in the bio-incubation experiments with SZVA as displayed in Figure 3 are similar to those observed for the MPP during meso-scale iron-fertilization experiments in the Southern Ocean [*Coale et al.*, 2004]. Our results illustrate that SZVA can indeed act as high-speed fertilizer and has the potential

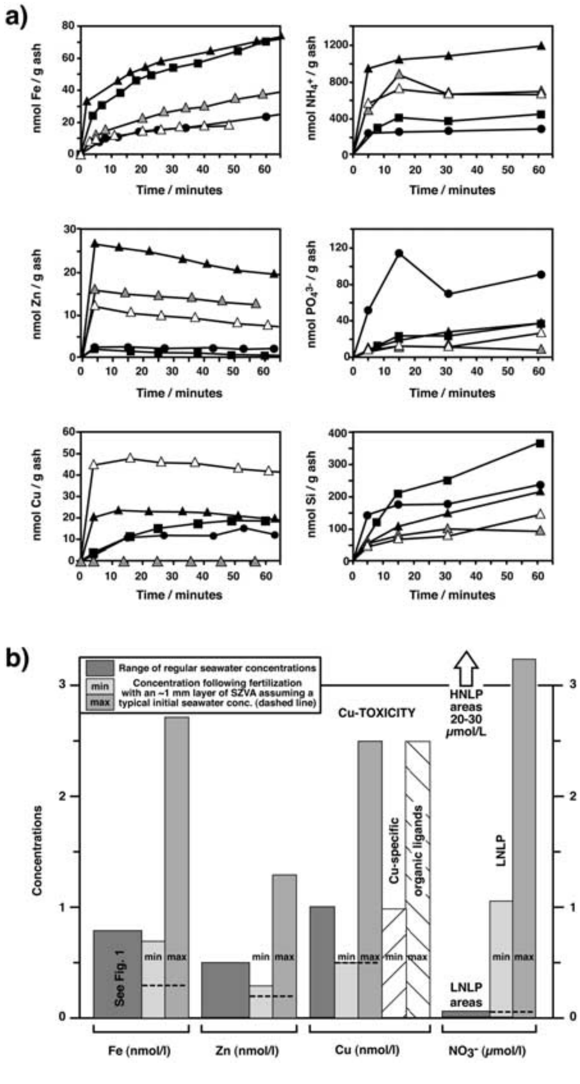

Figure 2. Effect of unhydrated subduction zone volcanic ash on seawater. (a) Results for nutrient release of unhydrated SZVA on contact with natural seawater from time-dependent geochemical experiments measured by means of Anodic Stripping Voltammetry and standard photometry. The SZVA stem from different eruptions of volcanoes in the Pacific Ring of Fire: Sakura-jima volcano in Japan sampled 11 June 1986 (on the campus of the Kagoshima university), 18 November 1987 (at the eastern foot of the volcano) and 12 June 1999 (again on campus) (white, grey and black triangles, respectively), Mt. Spurr sampled 18 August 1991 in Anchorage, Alaska (black circles) and permanently active Arenal volcano 1993 sampled at the foot of the volcano in Costa Rica (black squares). Natural seawater was sampled cleanly during cruises with large research vessels in the Antarctic and Atlantic Oceans. (b) Bar chart schematically displaying the effect on the nutrient budget of the upper section (mixed layer depth = 50 m) of the marine euphotic zone upon seaward deposition of a relatively thin, ~1 mm volcanic ash layer. The calculations are based on a short seawater-SZVA contact time of ~20 minutes as inferred from Figure 2a. Fixed nitrogen species were recalculated to nitrate. The bars denote the absolute range of surface ocean concentrations for individual trace metals and NO_3^- (see Figure 1). Concentrations of Fe, Zn, Cu and NO_3^- in LNLP and HNLP oceanic areas prior to fertilization and of Cu-specific organic ligands in oligotrophic regions governing the level of Cu-toxicity as discussed in the main text and Figure 1.

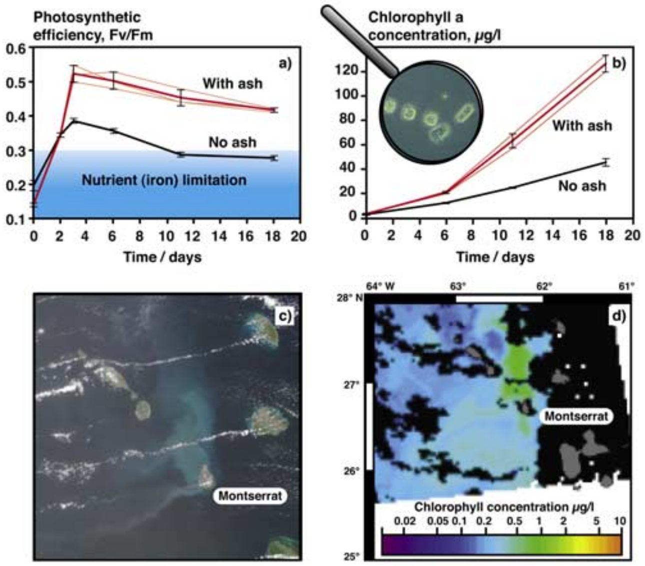

Figure 3. (a, b) Results from bio-incubation experiments with subduction zone volcanic ash and the diatom *Chaetoceros dichaeta* in natural seawater and (c, d) satellite data possibly indicating a phytoplankton bloom around ash-erupting Soufrière Hills volcano on Montserrat Island in the Lesser Antilles subduction zone. Figures 3a and 3b exhibit the increase of the photosynthetic efficiency Fv/Fm (Figure 3a) and chlorophyll *a* (biomass) concentrations (Figure 3b) during biogeochemical experiments with diatom phytoplankton (*Chaetoceros dichaeta,* shown in the reading-glass inset) in low-iron Antarctic seawater and SZVA as an iron-fertilizer in three of six experiments. Thin red lines display the results of single experiments, whereas thick red and black lines represent the geometric mean including error bars (s.d.). For nutrient limited conditions Fv/Fm is below ~0.3. Figure 3c shows an AQUA MODIS true colour space image showing Montserrat Island on 14th of July 2003 and a ~160 km by ~40 km sized greenish-blue seawater discolouration and Figure 3d processed SEASTAR SeaWiFs satellite data for the 17th of July illustrating that the seawater discolouration may result from an increase of chlorophyll concentration caused by a phytoplankton bloom.

to increase the MPP in at least iron-limited if not even all low-iron oceanic areas, making up the majority of the Earth's oceans (Figure 1). Natural manifestation for enhanced diatom growth following volcanic ash deposition is found in a drill core from the Southern Ocean showing a significant increase of the relative abundance of *Thalassiosira oestrupii* immediately after the deposition of a ~10 cm ash layer ~450 ka ago [*Kunz-Pirrung et al.*, 2002]. The association of a large number of ash layers and diatomites in the Danish mo clay formation [*Bøggild*, 1918] also suggests stimulation of diatom growth linked to volcanic ash deposition.

[14] However, whether volcanic particulate matter stimulates phytoplankton growth or not may depend on the presence or absence of toxic effects associated with the liberation of trace metals. Some metal ions are essential but can at elevated concentrations also have a negative (toxic) effect on the MPP. Such a 'Goldilocks' metal (not too little, not too much) [*Bruland and Lohan*, 2004] is Cu that can be released rapidly in significant amounts from SZVA (Figures 2a and 2b) and in general is more toxic to algae than Cd and Zn [*Bruland and Lohan*, 2004; *McKnight et al.*, 1981]. Cu is toxic as free cations but not when complexed with organic ligands, i.e. toxicity very much depends on the euphotic zone free-ion/complexed-ion ratio. In oligotrophic regions dominated by Cu-sensitive picoplankton [*Mann et al.*, 2002; *Morel et al.*, 2004] seawater concentrations of strong Cu-specific organic ligands are low (e.g. 1–2.5 nmol/l) [*Coale and Bruland*, 1988; *Moffet*, 1995], and free copper levels may be substantially and swiftly enhanced by SZVA eventually reaching toxicity (Figure 2b). On the other hand, phytoplankton species have different tolerances for and responses to Cu-toxicity [*Croot et al.*, 2000; *Mann et al.*, 2002; *Morel et al.*, 2004] and ash deposited in HNLP regions dominated by Cu-tolerant diatoms may have limited toxic effects. The toxic elements Pb and Cd, however, were only released in traces from SZVA and are unlikely to cause toxicity. In summary, our results illustrate that Cu-toxicity may be a relevant issue for the MPP upon seaward deposition of volcanic ash. A detailed understanding of this process, however, has to await results from open ocean bioassay experiments.

[15] Natural evidence for biological response to the seaward deposition of subduction zone volcanic particulate matter comes from satellite images and data of the bio-optical properties of seawater. A region of about 160 km by 40 km of greenish-blue seawater discoloration in the ash fall area around the active Soufrière Hills Volcano (Montserrat Island in the Lesser Antilles) was detected mid-July 2003 by the Moderate Resolution Imaging Spectroradiometer (MODIS) on board the AQUA and TERRA satellites (Figure 3c). Such a seawater discoloration in true color satellite images may be interpreted as a phytoplankton bloom. In order to verify this, we processed data provided by the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) on board the SEASTAR satellite (Figure 3d). The data indicate that the seawater discoloration may have been caused by a considerable increase in chlorophyll levels (~1 μg/l). However, the satellite data furthermore point to a significant raise of the surface reflectance at 555 nm, which could indicate suspended volcanic ash particles that in turn may bias the appraised chlorophyll value. Stokes' law estimates and data from the Pinatubo eruption [*Wiesner et al.*, 1995] suggest that this ash signal should have been removed by the time the image was acquired. Unfortunately, there is not sufficient ash reflectance data available for a quantification of the pseudo-chlorophyll signal and we encourage researchers focusing on the bio-optical properties of seawater to examine this phenomenon in more detail.

[16] The metabolism of marine biomass production is directly linked to the atmospheric (greenhouse) gas budget. Therefore, a massive stimulation of the MPP has the capability to cause a short- and long-term drawdown of atmospheric CO_2 and to release significant amounts of biogenic dimethyl sulfide (DMS) to the atmosphere forming a main precursor of cloud condensation nuclei [*Charlson et al.*, 1987; *Sarmiento*, 1993; *Watson*, 1997]. The combination of lower atmospheric CO_2 contents and a higher cloud frequency could ultimately provide a cooling component to the development of the global climate. It was argued recently that the 1991 eruption of the Pinatubo subduction

zone volcano enhanced the MPP in the Southern Ocean causing an atmospheric CO_2-drawdown associated with an excess O_2-pulse [*Frogner et al.*, 2001; *Keeling et al.*, 1996; *Sarmiento*, 1993; *Watson*, 1997]. Using our iron mobilization data (average for 20 minutes contact time) (Figure 2a, Table 1) and assuming a typical carbon/iron ratio of 10^5 for phytoplankton in Fe-limited areas [*Watson*, 1997], we calculated that rapid Fe-fertilization with, on average, $\sim 6.3 \times 10^{15}$ g of SZVA could have caused the estimated loss of CO_2 ($\sim 1.6 \times 10^{15}$ g of C applied to the Northern Hemisphere) following the Pinatubo eruption [*Sarmiento*, 1993]. This amount of ash, however, corresponds to ~35–48% of the material erupted during the 1991 Pinatubo eruption ($1.3-1.8 \times 10^{16}$ g) [*Oppenheimer*, 2004], much of which was deposited seaward. Integrating our new data from biogeochemical experiments with data from the literature therefore suggest that oceanic and atmospheric biogeochemical cycles may be affected swiftly and for years following major volcanic eruptions.

4. Conclusions

[17] Subduction zone volcanic ash has a substantial potential to alter the nutrient budget of the surface ocean and to stimulate the growth of diatoms and other phytoplankton in iron-limited and other low-productivity oceanic areas. Hence, oceanic fertilization with SZVA may play a vital role for the ocean-atmosphere gas interchange and ultimately the development of the global climate.

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