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**Role of volcanic ash
for the surface ocean
biogeochemical
iron-cycle**

S. Duggen et al.

The role of airborne volcanic ash for the surface ocean biogeochemical iron-cycle: a review

S. Duggen¹, N. Olgun^{1,2}, P. Croot², L. Hoffmann^{3,4}, H. Dietze², and C. Teschner^{1,2}

¹IFM-GEOMAR, Leibniz-Institute of Marine Sciences, Division Dynamics of the Ocean Floor, Wischhofstrasse 1–3, 24148 Kiel, Germany

²IFM-GEOMAR, Leibniz-Institute of Marine Sciences, Division Marine Biogeochemistry, Düsternbrooker Weg 20, 24105 Kiel, Germany

³Department of Plant and Environmental Sciences, Göteborg University, Carl Skottsberg Gata 22 B, 40530 Göteborg, Sweden

⁴Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

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Correspondence to: S. Duggen (sduggen@ifm-geomar.de)

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Abstract

Iron is a key micronutrient for phytoplankton growth in the surface ocean. Yet the significance of volcanism for the marine biogeochemical iron-cycle is poorly constrained. Recent studies, however, suggest that offshore deposition of airborne ash from volcanic eruptions is a way to inject significant amounts of bio-available iron into the surface ocean. Volcanic ash may be transported up to several tens of kilometres high into the atmosphere during large-scale eruptions and fine ash may encircle the globe for years, thereby reaching even the remotest and most iron-starved oceanic areas. Scientific ocean drilling demonstrates that volcanic ash layers and dispersed ash particles are frequently found in marine sediments and that therefore volcanic ash deposition and iron-injection into the oceans took place throughout much of the Earth's history. The data from geochemical and biological experiments, natural evidence and satellite techniques now available suggest that volcanic ash is a so far underestimated source for iron in the surface ocean, possibly of similar importance as aeolian dust. Here we summarise the development of and the knowledge in this fairly young research field. The paper covers a wide range of chemical and biological issues and we make recommendations for future directions in these areas. The review paper may thus be helpful to improve our understanding of the role of volcanic ash for the marine biogeochemical iron-cycle, marine primary productivity and the ocean-atmosphere exchange of CO₂ and other gases relevant for climate throughout the Earth's history.

1 Introduction

1.1 Purpose and structure of the review paper

Soils in volcanic areas have for thousands of years been known for their fertility (Schmincke, 2004) but the fertilising potential of volcanoes in the marine environment is poorly understood. Satellite images and drill core data from scientific ocean drilling

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illustrate that large amounts of volcanic ash have been deposited in the marine environment (Fig. 1). Yet relatively little still is known about the role of volcanoes for the surface ocean nutrient budget and how volcanic activity may affect marine primary productivity (MPP), carbon-cycles and climate in the Earth's history. Sufficient information is now available arguing that oceanic fertilisation with volcanic ash is a process that has largely been overlooked in marine sciences and that its significance for the marine biogeochemical iron-cycle might have been underestimated so far.

We provide an overview of the literature related to surface ocean fertilisation with volcanic ash. In an introduction, we briefly outline the young research field from a historic perspective, showing how ideas developed, complexity rapidly increased and how different research fields can provide important new information. Milestones and problems in improving our understanding of the role of volcanic ash for the surface ocean biogeochemical iron-cycle and whatever follows from that are highlighted, also drawing attention to important and unanswered research questions. The review is written in such a way that the reader can gain a quick overview from the introduction and leave it with that, or the more interested reader can move on to the other sections with an in-depth review of different chemical and biological aspects in this research field. We hope that the review will be inspiring and helpful for developing future research activities and to make an intriguing phenomenon of our planet more known to ocean scientists.

1.2 Giving birth to a new multi-disciplinary research focus – overview from a historical perspective

Since the early 20th century it was hypothesised, on the basis of growth experiments, that low concentrations or the lack of iron may limit phytoplankton growth in surface oceanic areas with little iron-supply from the continents (Gran, 1931; Harvey, 1937). About 50 years later ship-based experiments in the subarctic north Pacific confirmed that iron deficiency can limit marine phytoplankton growth (Martin and Fitzwater, 1988). Since then numerous studies tested the hypothesis and examined the role of artificial and natural oceanic iron fertilisation for the use of major nutrients, for global C-cycles

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and climate (Blain et al., 2007; Martin et al., 1990; Boyd et al., 2004, 2000; Cooper et al., 1996; Coale et al., 2004, 1996; Behrenfeld et al., 1996).

Although iron concentrations are very low (<1 nM) in vast areas of the surface ocean (De Baar and De Jong, 2001) (Fig. 2), the effects of iron-fertilisation are not of the same importance for the marine primary productivity (MPP) in all parts of the open ocean. Artificial and natural iron-fertilisation is particularly relevant for biogeochemical cycles in oceanic areas with excess macro-nutrients such as nitrate and phosphate that are not used up by unicellular algae in so-called high-nutrient low-chlorophyll (HNLC) or iron-limited areas. Addition of minor amounts of iron to surface waters of HNLC areas may cause massive phytoplankton blooms. In other oceanic areas, where the levels of both macro-nutrients and trace metals are relatively low (low-nutrient low-chlorophyll (LNLC) or oligotrophic areas such as the open ocean gyres), additional iron in the surface waters alone is unlikely to have the same immediate biological effects as in HNLC areas. In other oceanic regions, iron can control rates of nitrogen fixation (partly in connection with PO_4^{3-}) (Mills et al., 2004; Morel et al., 2004).

Soon after the discovery of iron-limitation in HNLC areas scientists started to think more deeply about natural sources of iron, including volcanoes. To our knowledge the person who first mentioned the possible significance of volcanic ash for the marine biogeochemical iron-cycle in the literature was Charles S. Spirakis from the US Geological Survey, in a short communication in EOS (Spirakis, 1991). He pointed to soluble salts and leachable iron found in volcanic ash but stressed that the amount of leachable iron from ash is not well known. Spirakis hypothesized that volcanic ash may be at least as good a source of soluble iron as iron-bearing desert dust added to the oceans. He also speculated that biotic productivity in iron-starved regions of the oceans should increase after addition of airborne volcanic ash and mentioned that the effect should be visible in satellite data. In 1993 Jorge L. Sarmiento linked the unexpected relative drawdown of atmospheric CO_2 in the Northern Hemisphere following the 1991 large-scale eruption of Pinatubo volcano (Philippines) to oceanic iron fertilization with volcanic ash (Sarmiento, 1993). He mentioned the unfortunate luck in the lack of an

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ocean colour imager available at that time, as the according increase in MPP would likely have been visible from space. Sarmiento made some simple calculations as to the amount of iron required from the Pinatubo volcanic matter but these were based on the bulk composition of the material that did not take into account how the iron was bound (e.g. in soluble salts or less soluble silicate structures) (Spirakis, 1991). In 1997 Andrew Watson drew the attention to an extra atmospheric oxygen pulse emanating from the ocean in the Southern Hemisphere (Keeling et al., 1996), eventually associated with the post-Pinatubo eruption atmospheric CO₂-drawdown. He linked this to iron-fertilisation with volcanic ash in the iron-limited Southern Ocean, which is a major HNLC area (Watson, 1997). Watson further stressed that iron-fertilisation with volcanic ash can not only cause short-term perturbations of the atmospheric CO₂ but may also have long-term effects – on the order of thousands of years – through changes in the inorganic to organic carbon rain ratio associated with diatom blooms. In his iron-flux calculations he assumed (based on measurements of aeolian dust) that 1% of the bulk iron content is soluble and thus bio-available for uptake in marine phytoplankton. In order to link oceanic Fe-addition to C-cycles, Watson used the molar C:Fe ratio of phytoplankton observed in iron-limited areas, which is on the order of 10⁵. This large number stresses that even relatively small amounts of iron added to the surface ocean may have a strong impact on the MPP and C-cycles. In a more recent paper it was proposed that fertilisation by volcanic fallout may be partly responsible for productivity feedback and the termination of global warmth at the Paleocene/Eocene boundary (Bains et al., 2000). This implies that surface ocean iron-fertilisation by volcanic ash might be among the essential processes in shaping the Earth's climate history.

Until the year 2000 the discussion of the role of volcanic ash for the surface ocean iron-cycle was scattered in short communications or minor comments in articles focussing on other issues. Although restricted to ideas, speculations and hypotheses these publications were inspiring and helped giving birth to a new research focus. Results from the first study that linked the release of iron and other nutrients from volcanic ash to the surface ocean nutrient budget was presented during the 2000 Goldschmidt

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Conference (Frogner et al., 2000), followed by a publication a year later by a group of authors with a deep-going background in geochemistry and volcanology (Frogner et al., 2001). Until then ash-leachate studies that included iron in examining the release of trace metals and various chemical compounds dealt with onshore processes such as the impact on the environment (e.g. health, livestock, vegetation, lake water) and chemical processes (e.g. chemical weathering of volcanic ash and soil fertility) (Witham et al., 2005) and references therein). Moreover, in these leaching experiments seawater was rarely used but instead distilled/deionised water or acidic or alkalic solutions. Frogner et al. (2001) demonstrated in geochemical experiments with volcanic ash (sieved to 44–74 μm size) and natural seawater that an ash sample from the Icelandic Hekla volcano releases an array of macro- and micro-nutrients such as phosphate, silica and various trace metals (e.g. iron) relevant for marine phytoplankton growth. The flow-through experiments were designed to monitor the release of these elements from volcanic ash in seawater on an hour-scale with the first solution taken for measurements after 45 min. Most of the nutrient mobilisation, however, took place within these 45 min contact time, indicating a relatively short timescale release of nutrients from volcanic ash in contact with water. Frogner et al. (2000) argued that dissolution of soluble salt coatings found on the surface of ash particles were most likely responsible for the relatively swift release of nutrients. Based on their results, they discussed the fertilising potential of the 1991 Pinatubo eruption as a possible cause for the CO_2 -drawdown that followed in the years after. In the following two years other authors provided statistical evidence from ice core data for a causal connection between volcanism and millennial climate change (Bay et al., 2004, 2006). It remained unclear, however, whether volcanism caused climate change (e.g. through increased iron supply to large surface ocean areas) or, vice versa, climate change rapidly influenced volcanic activity (e.g. through sea level change and changing pressure conditions in magma chambers of coastal volcanoes).

More recently, Duggen et al. (2007) provided new constraints on the role of volcanic ash on the surface ocean biogeochemical iron-cycle. Time-dependent geochemical experiments with natural seawater and five volcanic ash samples from three subduction

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zone volcanoes (Arenal in Costa Rica; Mt. Spurr in Alaska and Sakura-jima in Japan) demonstrated a rapid (minute-scale) release of iron and an array of other nutrients. The study focused on volcanic ash from volcanoes in subduction zones as these host most of the subaerially active volcanoes on Earth that can erupt enormous amounts of volcanic ash through explosive eruptions as high as 30–50 km into the stratosphere (Sigurdsson et al., 2000). The authors used bulk (i.e. unsieved) ash samples and included an iron-complexing organic ligand added to Antarctic seawater, mimicking the existence of siderophores in natural surface ocean water. With their geochemical experiments, Duggen et al. (2007) showed that significant amounts of iron are released from volcanic ash at time-scales during which ash particles sink through the sunlit part of the surface ocean where phytoplankton thrives (the euphotic zone). The observed very rapid release of iron in geochemical experiments is consistent with a detailed surface analysis of ash particles from the same year (Delmelle et al., 2007). The study confirms and demonstrates the existence of thin (<10 nm) coatings of soluble salts found on the surface of ash particles. The salt coatings contain iron and are proposed to be formed through interaction of the ash particles with volcanic gases (e.g. HCl, HF) during the eruption.

The first results from biological experiments with Antarctic seawater and volcanic ash (from Arenal volcano) as a source for iron were presented in the same year by Duggen et al. (2007). The bio-incubation experiments were performed under iron-limited conditions with an Antarctic diatom species (*Chaetoceros dichaeta*) that is common in the iron-limited (HNLC) Southern Ocean. Over the course of 18 days two key biological parameters, namely chlorophyll-*a* (Chl-*a*) concentration (as a measure for biomass) and the photosynthetic efficiency (as a measure for the efficiency with which algae can use sunlight for photosynthesis) were monitored. Both parameters were significantly higher in the experiments where phytoplankton grew in volcanic-ash-fertilised seawater, compared to control experiments in which the seawater was not fertilised with volcanic ash. These experiments were the first to show that phytoplankton in iron-limited areas are able to utilize iron from volcanic ash to build up biomass. Duggen

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et al. (2007) stressed that the addition of volcanic ash to the surface ocean can either be positive (e.g. through iron addition) or negative through release of toxic metals (e.g. copper or other metals) on phytoplankton growth, so that volcanic ash injected to the surface ocean may have different effects on different algae species. More experiments with other species from other oceanic regions have been performed, indicating that different phytoplankton species indeed show different response to volcanic ash addition (L. Hoffmann, personal communication, 2008).

Scientists have also searched NASA satellite archives for natural evidence for marine biological response to volcanic fallout. Satellite techniques such as MODIS (Moderate-Resolution Imaging Spectroradiometre) and SeaWiFS (Sea-viewing Wide Field-of-View Sensor) for obtaining true colour images and monitoring the bio-optical parameters such as Chl-*a* of the surface ocean have only been available for about a decade, so the information is still limited (see summary of satellite techniques available for this purpose in Langmann et al., 2009). In 2004 Uematsu et al. provided direct natural evidence for a marine fertilisation event in the aerosol fallout area of the 2000 eruption of Miyake-jima volcano offshore Japan (Uematsu et al., 2004). Enhancement of phytoplankton growth in the fallout area of Miyake-jima was inferred from an increase in surface ocean chlorophyll-*a* (Chl-*a*) levels, detected using the satellite-based SeaWiFS tool. The increase of the MPP, however, was associated with offshore deposition of ammonium-sulphate aerosols formed from NH₃ and SO₂ gases released by the volcano. Therefore the stimulation of phytoplankton growth in the oligotrophic oceanic area downwind of Miyake-jima was caused by fertilisation with fixed nitrogen (ammonium-sulphates) rather than iron.

Greenish-blue seawater discolourations, usually interpreted as phytoplankton blooms, were repeatedly observed in the vicinity of erupting Souffrière Hills volcano on Montserrat (Lesser Antilles) using MODIS, for example in July 2003 (Duggen et al., 2007). SeaWiFS data also point to a significant increase in Chl-*a* levels within the ca. 160 km by 40 km large discoloured oceanic area. The problem, however, is that there is also evidence for increased reflectance at wave-lengths where Chl has an absorp-

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tion minimum. It thus still is unclear how much of the chlorophyll signal is a true signal or a pseudo-chlorophyll signal arising from volcanic particulate matter in the surface ocean or in the atmosphere. It further remains unclear whether a possible phytoplankton bloom visible in the vicinity of Montserrat from space is associated with the release of fixed nitrogen (NO_3^- , NO_2^- or NH_4^+) from volcanic ash or iron or both, as the oceanic area around Montserrat is thought to be oligotrophic (LNLC). In the meantime some more satellite true colour photos showing seawater discolouration associated with volcanic fallout have been found, the causes of which are under examination (F. Prata, 2008, personal communication at the IAVCEI conference in Reykjavik). Notably, data from seawater samples collected during a cruise east of Sicily in the ash fall-out area of the large-scale 2001 eruption of Etna volcano (see Fig. 1) show strongly increased concentrations of dissolved iron (up to several hundred nM) and other trace metals that are reported to be linked to enhanced Chl-*a* levels (Randazzo et al., 2009).

A recent satellite study provides the first direct natural evidence that volcanic ash fall-out can cause iron-fertilisation in an iron-limited oceanic (HNLC) area and a phytoplankton bloom (Langmann et al., 2009). Using different satellite techniques such as MODIS and SeaWiFS the authors demonstrate a causal connection between the eruption of Kasatochi volcano in the Aleutian subduction zone and a large-scale phytoplankton bloom in August 2008 in the northeast subarctic Pacific commencing soon after the onset of ash fall-out into the surface ocean. Worth noting is that this first-time observed natural evidence of volcanic-ash-induced iron-fertilisation occurred in the same area where Martin and Fitzwater (1988) took water samples in the Gulf of Alaska at the Ocean Station PAPA for their biological experiments to confirm that iron-deficiency can limit marine phytoplankton growth.

Another geochemical study examined the release of biologically relevant elements, including iron, from volcanic ash on contact with seawater and ultrapure water (Jones and Gislason, 2008) by means of flow-through experiments similar to Frogner et al. (2001). Most of their volcanic ash samples (sieved to 45–125 μm size) stem from subduction zone volcanoes (volcanoes Galeras in Columbia; Lascar in Chile; Soufrière

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Hills on Montserrat; Mount St. Helens in the USA; Sakurajima in Japan; Santiaguito in Guatemala) and one comes from the Iceland hotspot (Hekla volcano). Jones and Gislason (2008) also determined the pH and found an initial strong drop in the solute (including seawater) for some ash samples. As discussed in more detail further below, the drop of pH may be an important issue for the oceanic iron-cycling, for two reasons: First, pH drop can potentially occur in those parts of an ash fall-out area where the ash load in the otherwise pH-buffered surface ocean is high and affect surface ocean iron solubility, e.g. in the proximity to the volcano (direct pH effect). Second, pH drop in fog and cloud water in contact with volcanic ash in the atmosphere may strongly increase the amount of iron mobilised from volcanic ash through enhanced glass dissolution, so that it may be important whether the ash is transported into the surface ocean through dry or wet deposition (indirect pH effect).

Jones and Gislason (2008) also drew attention to the post-sampling decay of the soluble salt coatings on the surface of ash particles, which occurs even if the samples are stored dry. Further constraints for the salt coating decay were recently provided by a systematic study of numerous pristine ash samples from subduction zone volcanoes encircling the Pacific Ocean (Olgun et al., 2009). The decay appears to affect samples more than a few years old and is expressed by a tendency of decreased Fe-mobilisation with increasing age of the sample. The issue would be important for future flux estimates of iron into the surface ocean, both on a regional, short-term scale (e.g. during single major eruptions) or on a basin-wide long-term scale (e.g. for an oceanic basin over geological timescales).

Estimates of the flux of iron from volcanic ash to the surface ocean are an important component in improving our understanding of the role of volcanic ash for the oceanic iron-cycle. Iron-release data have been used to calculate the possible increase of iron concentrations in the surface ocean through the deposition of ash from subduction zone volcanoes. It was inferred to be on the order of a few nM (nmol/kg) for a 1 mm ash layer (Duggen et al., 2007), which is enough to trigger a massive phytoplankton bloom in an iron-limited (HNLC) oceanic area (>2 nM Fe-increase) (Wells, 2003).

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Worth noting here is that scientific ocean drilling reveals that volcanic ash layers in the open ocean can have thicknesses on the mm-, dm- and even up to the metre-scale and that these also occur in iron-limited HNLC areas (Straub and Schmincke, 1998). This implies that volcanic ash fall-out has the potential to swamp the surface ocean with iron at least within the ash fall-out area. Iron fertilisation may in such case not be restricted to the ash fall-out area, as iron-fertilised surface ocean water can be distributed with oceanic currents away from the site of iron-injection. It is, however, unclear how much of the iron injected by single major eruptions can stay in solution and in a form that is bio-available, which will much depend on iron speciation and the presence of iron-complexing organic ligands (as discussed in more detail below).

Recent estimates for the Pacific surface ocean indicate that the flux of iron from volcanic ash is potentially within the same order of magnitude as the flux of iron from aeolian dust (Olgun et al., in prep.). Furthermore, Olgun et al. infer that subduction zone volcanoes contribute the majority of the iron-load because: 1) the flux of SZVA to the surface Pacific ocean is much higher than that of HSVA and 2) subduction zone volcanic ash (SZVA) has a higher iron-mobilisation potential compared to hotspot volcanic ash (HSVA), most likely linked to characteristics of the subduction zone volcanic gas system through enhanced Cl and F contents and thus ultimately to the subduction of oceanic lithosphere at convergent plate margins. Olgun et al. also highlight that volcanic ash and aeolian dust deposition is unevenly distributed. Therefore the relative role of these atmospheric iron sources for the iron-cycle of the Pacific surface ocean (covering about half of the Earth's surface and hosts about 70% of the iron-limited, HNLC oceanic areas) will much depend on the short- to long-term temporal and spatial distribution patterns of these atmospheric components. The flux estimates, however, suggest that volcanic ash is a major and hitherto underestimated component in the millennial-scale atmospheric input of iron to the surface ocean, especially in the Pacific Ocean.

Finally worth noting is that volcanic ash carrying soluble (and bio-available) iron is not injected into surface ocean water by direct fallout during volcanic eruptions alone.

A recent piston core study of sediments in the Atlantic sector of the Southern Ocean suggests that ash can be deposited on sea ice that later can be transported more than 1000 km away from the site of deposition (Nielsen et al., 2007). It is possible that volcanic ash deposited and preserved on sea ice maintains the full potential to release soluble and bio-available iron upon ice melting so that iron-fertilisation with volcanic ash may occur in the open ocean, far away from the source volcano and the original ash-fall area.

2 What is volcanic ash?

Freshly erupted volcanic ash (pristine or juvenile ash) is different from fossil volcanic ash and aeolian dust. Pristine volcanic ash particles have iron-bearing soluble salt coatings and can through volcanic eruptions be transported directly into the surface ocean and rapidly release soluble and bio-available iron (Delmelle et al., 2007; Duggen et al., 2007; Jones and Gislason, 2008; Frogner et al., 2001). Fossil volcanic ash was deposited on land, and has been subject to hydrological and soil processing since then, and may be taken up by winds and become a component of aeolian dust. Fossil ash, however, differs significantly in terms of chemical behaviour on contact with seawater, as the original soluble salt coatings should have been washed away due to rain.

Volcanic ash is produced in the course of fragmentation processes during explosive volcanic eruptions. A general term for fragmented volcanic material is “tephra”, the classification of which is based on the grain size, distinguishing three main types: 1) ash (particles below 2 mm down to the micrometer-scale), 2) lapilli (2–64 mm), and 3) bombs and blocks (>64 mm) (Schmincke, 2004; Fisher and Schmincke, 1984). Due to the granulometric classification the term “volcanic ash” does neither include information about a particular volcanic process forming the ash nor about its shape or composition. Volcanic ash is produced by both subaerial or submarine volcanic eruptions. In the current paper we focus on the significance of airborne volcanic ash produced by explosive eruptions on land and that may reach the surface ocean after atmospheric

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transportation.

The transport and dispersal of airborne volcanic ash is affected by the type and scale of the eruption (e.g. Strombolian, Hawaiian, Plinian etc.), wind directions, and size and density of ash particles. Ash particles fall out of a volcanic ash plume (Fig. 3) according to their settling velocities, which is related to their density and size. As the distance from the source increases, maximum particle size and grain size distribution generally decreases (Walker and Craosdale, 1972). However, sorting is rarely perfect since very small particles commonly become agglutinated (e.g. through electrostatic forces and moisture) and therefore may be deposited together with larger particles. The median diameter found in submarine ash layers from subaerial eruptions commonly vary between 125 to 63 μm and smaller (Pedersen and Surlyk, 1977). Fragments with small air-fall velocities compared to wind strength may encircle the globe several times before settling to ground (e.g. micrometer-size ash particles from major volcanic eruptions such as Pinatubo 1991).

The chemical composition of airborne volcanic ash ranges from mafic (relatively high MgO and FeO but low SiO₂ contents) to silicic (relatively low MgO and FeO but higher SiO₂). The bulk composition of volcanic ash is defined by the proportions and compositions of individual vitric fragments (glass shards, pumice), pyrogenic minerals, lithic particles (pieces of pre-existing rocks) and salt coatings (Fisher and Schmincke, 1984; Óskarsson, 1981; Delmelle et al., 2007). Glass shards are particles of the chilled, fragmented melt and form angular and irregular fragments, partly with extraordinarily large surface-to-volume ratios (Fig. 4) and are typically a dominating component of volcanic ash (Fisher and Schmincke, 1984). Pyrogenic minerals are crystals that crystallised in the magma prior to the eruption and mainly include silicate minerals such as amphibole, biotite, feldspar, olivine, pyroxene and quartz, depending on the chemistry of the magma. Minerals are more abundant in the grain size range of about 2 mm and 63 μm and are generally absent below 10 μm , whereas glass shards can be much smaller like aerosols. Lithic particles may include fragments of volcanic rocks from previous eruptions and/or the subvolcanic basement rock and may therefore be of any

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crustal origin (Fisher and Schmincke, 1984). Silicic ash, however, is more widespread than mafic ash: 1) due to a potentially greater explosivity of volcanic eruptions involving SiO₂-rich, high-viscosity magmas (Schmincke, 2004) and 2) because SiO₂-poor components such as ferromagnesian minerals (e.g. olivine, clinopyroxene) have higher densities than the coexisting, SiO₂-rich glass and will tend to settle faster than the glass shards (aeolian fractionation) (Larsson, 1937; Middleton, 2003). All solid particles found in volcanic ash plumes may during the eruption interact with surrounding volcanic gases to form iron-bearing soluble salt coatings.

3 Processes that transfer volcanic iron into soluble and bio-available form

There are two principal ways how iron in volcanic ash can be transferred into soluble forms and thus become bio-available in the surface ocean (Fig. 3): 1) formation and dissolution of soluble salt coatings on the surface of ash particles and 2) dissolution of glass shards in the ash in contact with a solute. Soluble salt coatings may dissolve either in direct contact with seawater (dry deposition) or in contact with cloud water which eventually rains into the ocean (wet deposition). Below we briefly outline these two principal ways of Fe-mobilisation.

The first step in the formation of soluble salt coatings apparently is the unmixing of an iron-bearing (non-silicate) fluid phase from a silicate magma rising to shallow crustal levels beneath a volcano. Iron and other heavy metals such as Cu and Zn are transported as chlorine complexes (e.g. FeCl₂⁰) into the fluid phase, which to some extent links the iron- to the chlorine-cycle for the formation of soluble salts on ash particles surfaces. In the course of an explosive volcanic eruption the iron-bearing fluid phase is erupted together with the fragmented silicate melt, contributing to the formation of volcanic gases and aerosols (e.g. tiny salt crystals) (Fig. 3). During cooling the gases may condense on and the aerosols may adsorb to the surface of ash particles in the plume of a volcanic eruption, forming iron-bearing soluble salt coatings (Óskarsson, 1980). In addition, the surface of the ash particles may react with volcanic gases such

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as HCl and HF that are aggressive to silicates, especially the glass shards, at various temperatures in the eruptive plume (Delmelle et al., 2007). As iron usually is a major element in volcanic glass, the process should transfer further iron into soluble salts such as halogenides. Reaction with oxygen, volcanic SO₂ or H₂S may transform the halogenides to oxides, sulphates or sulphides (Óskarsson, 1980, 1981). In the course of a volcanic eruption, the salts on the surface of ash particles may thus go through several cycles of dissolution and precipitation, ultimately forming coatings of iron-bearing soluble salts (for a more detailed discussion of these processes see Olgun et al., and references therein). The salt coatings have been visualised recently by microscopic methods (Fig. 4e, f) (Delmelle et al., 2007). As halogenides, oxides, sulphates and sulphides have different solubilities and variable Fe-contents, these salts should dissolve at different timescales on contact with water, eventually releasing Fe dependent on the nature of the solute (e.g. pH, presence of organic ligands).

Glass shards are frequently found in volcanic ash and glass dissolution on contact with water is also likely to play a role for the marine biogeochemical iron-cycle. Iron is usually found in major element concentrations in metastable volcanic glass so that even partial dissolution of the glass shards may transfer significant amounts of iron into solution. Glass dissolution rates in a solute, however, are dependent on various chemical and physical parameters (Wolff-Boenisch et al., 2004a, b; Flaathen et al., 2008). The dissolution rates are relatively slow in seawater and therefore the iron-release behaviour, while volcanic ash sinks through the euphotic zone, is probably dominated by dissolution of soluble salt coatings (Jones and Gislason, 2008; Duggen et al., 2007). Very little, however, is known about the mobilisation of iron from volcanic ash that interacted with cloud water, which is discussed in more detail below.

4 Chemical behaviour of volcanic ash on contact with water

Constraints on the iron-mobilisation behaviour of volcanic ash mostly stem from leaching experiments, where ash is brought in contact with an aqueous solution. Due to

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coatings of soluble salts that contain iron (Delmelle et al., 2007) it is crucial to conduct leaching experiments with pristine (unhydrated or dry) volcanic ash, i.e. ash that has not been in contact with water after deposition and prior to the experiment. Unfortunately, such ash material is relatively rare in comparison to fossil ash that has been exposed to water (rain or groundwater). Fossil ash is unsuitable for leaching studies examining the release of nutrients in the euphotic zone. Laboratory leaching studies can still provide valuable information as we know of only one field study where surface ocean water samples were collected within an ash fall-out area of an erupting volcano. This was done during the 2001 eruption of Etna volcano (Fig. 1) and the seawater samples show strong increases of dissolved iron concentrations up to ca. 650 nM down to 300 m below sea level (Randazzo et al., 2009).

Leaching experiments with pristine volcanic ash and water or aqueous solutions have been performed for decades (a detailed review was provided by Witham et al., 2005). Until recently leaching experiments focussed on landward environmental issues such as air pollution and contamination of pasture, soil, groundwater and lakes and the consequences for human health and livestock. The environmental problems arising from volcanic ash fall-out on land or into fresh water systems were mainly associated with the release of halogenides (especially F^-), heavy metals and toxic complexes (Witham et al., 2005; Frogner Kockum, 2006, and references therein). Other studies investigated the release of such components to examine processes in plumes of volcanic eruptions (plume/gas proxies). Iron, however, has only gained limited attention in these experiments and only very recently studies investigated the release of iron together with other elements on contact with seawater and on timescales comparable with the surface ocean residence time of ash sinking through the euphotic zone.

4.1 The iron-release behaviour of volcanic ash

As outlined in Table 1, so far three main different laboratory approaches have been used to determine the release of iron from volcanic ash in a solute (seawater or ultra-pure water): 1) agitation experiments, 2) flow-through reactor experiments and 3) ex-

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periments with iron concentrations determined in situ in the solute. In the first case the ash is shaken in a solute, in the second the solute is slowly pumped through a batch of ash. In both cases the solute is separated from the ash by filtration and submitted to analysis of Fe and other elements (e.g. by ICP-AES). In the course of the in situ experiments ash is added to a solute and the changes in Fe-concentrations are measured as a function of time directly in the solute (e.g. by electrochemical stripping voltammetry). The amount of ash required for the different experimental setups ranges from several gram (agitation and flow-through experiments) down to several tens of microgram (in situ measurements). In the following, we summarise the results of relevant studies available in the literature. Subsequent subsections focus on issues that (as we think) currently merit a more in-depth discussion. Beyond the experimental setup and analytical method for iron-determination the experiments are distinguished by involving: 1) ash samples from different volcanoes in distinct tectonic settings (e.g. subduction zones versus hotspots), 2) sieved or non-sieved (bulk) ash samples, 3) variable ash-to-seawater ratios, 4) different contact times between the ash and solute, 5) a variation of the type of solute (natural or artificial seawater, ultrapure water, acidified or alkaline water), and 6) absence/presence of organic ligands.

A key result from these minute- to day-scale experiments is that iron is always released from pristine volcanic ash in amounts that can alter the surface ocean Fe-budget. In general, pristine ash samples from subduction zone volcanoes release between several 10 to several 100 nmol of Fe per gram of ash in ultrapure and seawater (Table 1). Exceptionally high iron-release such as for subduction zone volcanic ash from the Galunggung volcano, however, seems to be restricted to acidified solutes. The data available also point to systematic differences in the iron-release behaviour of ash from subduction zones (SZVA) and hotspots (HSVA), which is important to keep in mind for future estimates of the flux of Fe from volcanic ash into the surface ocean. A discrepancy with relatively high Fe-release of the 2000 Hekla HSVA sample used in two different studies (Frogner et al., 2001; Jones and Gislason, 2008) seems to be caused by sampling of the ash together with snow, as discussed in more detail below.

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There is, however, a tendency that ash releases significantly more iron in experiments with ultrapure and especially acidified ultrapure water (Table 1), indicating that reaction with cloud water and thus wet deposition may lead to a substantial increase in iron-mobilisation of volcanic ash. The iron-release data now available suggest a global value in the range of 100–400 nmol Fe for the dry deposition of each gram SZVA, which is likely to be a useful parameter for global models of the surface ocean biogeochemical iron-cycle.

4.1.1 Decay of soluble salt coatings? – Implications for flux estimates

Jones and Gislason (2008) recently raised concerns regarding the stability of soluble salt coatings on ash particle surfaces. Using the same flow-through reactor they re-analysed the Hekla 2000 sample also used in experiments by Frogner et al. (2001) and found that it released substantially less iron in year 2007 (ca. 7–9 $\mu\text{mol Fe/g ash}$) compared to year 2000 (ca. 36 $\mu\text{mol Fe/g ash}$) experiments. Frogner et al., however, had sieved the sample to 44–74 μm , whereas Jones and Gislason sieved the sample to 45–125 μm , so that there was significant differences in the particle size analysed. Jones and Gislason also mention that ash particles $<100 \mu\text{m}$ show a strong increase in element-release, which alone could explain why the 2000 Hekla sample released significantly more Fe about 5–6 years earlier.

Further constraints on the decay of soluble salt coatings on ash particles come from experiments with a larger number of subduction zone volcanic ash samples (Olgun et al., 2009). Older samples tend to release iron by a factor of up to ten less than younger samples. For example, four samples from Sakura-jima volcano, sampled since the mid-1980s, show a linear decrease of Fe-release with increasing age, which is largely mimicked by four samples from Arenal volcano (which basically is a two-point line though). The Sakura-jima ash samples, however, suggest that the Fe-mobilisation potential (and thus probably element-mobilisation potential in general) of an ash sample from a subduction zone volcano may be reduced to about 50% after 10 years of storage and to about 10% after ca. 20–25 years (Olgun et al., 2009). Although the

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number of pristine HSVA samples so far analysed is relatively low, it seems that the effect is not observed for ash samples from hotspot volcanoes (e.g. Iceland, Hawaii) and limited to ash samples from subduction zone volcanoes. The decay phenomenon indicated for SZVA may be associated with transformation of Fe-bearing halogenides on the surface of ash particles into less soluble salts, e.g. through loss of Cl and F into the vapour phase and formation of Fe-oxides (e.g. goethite). The available data show that the possible influence of salt coating decay needs to be kept in mind for the use of decade-old versus young ash samples, as the phenomenon could introduce an order of magnitude error (too low) into estimates of the flux of iron into the marine environment.

4.1.2 Sampling with snow

A way to contaminate pristine ash samples is by collection with snow as snow may contain various components other than crystallised clean water. This may especially be an issue in volcanic areas, as airborne snow is capable of scavenging substantial amounts of volatiles from the air in the plume of a volcanic eruption. Snow deposited during the 2000 eruption of Hekla volcano was analysed and found enriched in most trace elements. For example, the snow contained up to $163 \mu\text{g/g}$ Al, up to 990 ng/g Zn, up to $1260 \mu\text{g/g}$ F^- and had, when molten, pH values as low as 2.5 (Moune et al., 2006). Unfortunately, iron concentrations of the snow were not determined but are likely to have been elevated also.

The Hekla 2000 volcanic ash sample repeatedly used for geochemical iron-release experiments, however, shows an anomalously high Fe-release behaviour with ca. $36 \mu\text{mol Fe/g}$ ash (Frogner et al., 2001) and ca. $7\text{--}9 \mu\text{mol Fe/g}$ ash (Jones and Gislason, 2008) in flow-through experiments with seawater. The 2000 Hekla ash sample was collected together with snow, kept at sub-zero temperatures and then freeze-dried. During the freeze-drying process components contained in coexisting snow will ultimately end on the surface of the ash particles. It is therefore well possible that the high Fe-release of the Hekla 2000 ash sample is associated with snow-contamination. Collection of pristine ash samples together with snow or ice may thus strongly affect

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the quality of ash samples and yield unrepresentative results in leaching experiments.

4.1.3 Significance of the ash-to-seawater ratio – proximal versus distal ash fall-out

Geochemical experiments examining the release of iron in (sea)water have been performed with different ash-to-water ratios. These range from about 1:0.5 to 1:1000, corresponding to very high to very low ash loads (Table 1). So far, no clear correlation between the Fe-release behaviour and the ash-to-seawater ratio exists. The reason may be that uncertainties arising from different experimental setups with different solutes and contact times may mask possible systematic ash-to-seawater-ratio-dependent differences in the iron-release behaviour of volcanic ash. No general rule, however, can be provided as to which ash-to-water ratio is correctly used in geochemical experiments the ash load in an ash fall-out area varies with volcanological and atmospheric parameters. Among these are: 1) the scale of the volcanic eruption, which includes the erupted ash volume and the altitude to which the ash is transported into the atmosphere (up to 50 km), 2) the rate at which the ash is expelled from the volcano, 3) the wind speed in combination with the grain size spectrum of the ash particles, which defines how far the particles travel before being deposited in the surface ocean, and 4) the distance from the volcanic source (proximal or distal) (Fig. 3).

In general the offshore ash load in a given oceanic area is high if the volcanic mass flux is high (high volume erupted during a short period) during low wind speed conditions and the oceanic area is located close to the volcano (e.g. a proximal coastal oceanic area). Alternatively, the ash load in a given location would be low the smaller the scale of the eruption and the slower the rate of ash release, the stronger the winds and the further the oceanic area is located away from the volcanic source (e.g. a distal open oceanic area). For example, the ash layer deposited in the coastal region near erupting Mt. Pinatubo (1991) was about 10–20 cm thick (Wiesner et al., 2004), which (with a density of ca. 2.5 g/cm³ and a porosity of ca. 30%) corresponds to an ash load of about 2500 to 5000 g/dm². Assuming 50 m mixed layer depth, i.e. if equilibrated

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with a 50 m water column, this ash load corresponds to an ash-to-water ratio of roughly 1:200 to 1:100. During much larger eruptions, however, the ash load in coastal areas near the volcano can be clearly higher, i.e. ash layer thickness on the metre-scale (e.g. during the Toba super-eruption ca. 75 ka ago (Oppenheimer, 2002)). Evidence for the thickness of ash layers in the open ocean comes from scientific ocean drilling, where it has been observed that volcanic ash layers, even hundreds and thousands of kilometres away from the coast can have thicknesses on the millimetre-, centimetre- and decimetre-scale, occasionally even up to the metre-scale (Rea et al., 1995; Kutterolf et al., 2008). Millimetre and metre thick ash layers yield, respectively, an ash load of ca. 25 g/dm² and 25 000 g/dm², which roughly correspond to ash-to-seawater ratios of 1:20 000 and 1:20, if referenced to a 50 m water column. Very low ash-to-seawater ratios are expected for the deposition of the very fine fraction of volcanic ash that can be kept suspended in the atmosphere for months or years and reach very remote areas of the surface ocean. Nevertheless, the iron-release potential of these very fine, basically aerosol-size particles may be considerable due to their very high surface-area-to-volume ratio. Since most of the 1991 Pinatubo volcanic ash was deposited in the South China Sea (Wiesner et al., 2004), it may be possible that the hypothesized iron-fertilisation effect of the Southern Ocean with Pinatubo ash (Sarmiento, 1993; Watson, 1997) was associated with deposition of suspended very fine ash (F. Prata, personal communication).

Several authors have argued that their experiments were designed to mimic the settling of ash through the surface ocean. The calculations above show that the ash-to-seawater ratio chosen can be very variable, depending on the process considered. An ash-to-seawater ratio of 1:8 used in the flow-through experiments of Frogner et al. (2001) and Jones and Gislason (2008) is representative for a very high ash load relevant for the deposition of a metre-scale ash layer, which is very rare in the open ocean but may be found in coastal areas in the vicinity of very large-scale volcanic eruptions. The 1:400 ash-to-seawater ratio used in in situ experiments of Duggen et al. (2007) and Olgun et al. (2009) are closer to ash loads linked to centimetre-

scale ash layers frequently found in the open ocean. Experiments at very low ash-to-seawater ratios (e.g. well below <1:500) that are likely to be associated with ash layer thicknesses on the millimetre-scale have rarely been performed (Table 1). It is tempting to extrapolate results from geochemical experiments to lower (and higher) ash-to-seawater ratios and thus ash loads. One should, however, be aware that extrapolation by orders of magnitudes may not be feasible, especially for experiments with high ash-to-seawater ratios. In such experiments effects of re-adsorption of Fe to the surface of ash particles and solubility limitations (e.g. due to pH-dependent Fe-solubility and the presence/absence of organic ligands) are likely to introduce large errors that would propagate into the extrapolation. In general, it would be useful if the amount of ash and (sea)water chosen for a geochemical experiment attempts to mimic processes in nature. For dry deposition, experiments with high ash-to-water ratios would be useful to examine the effect of large-scale eruptions in coastal oceanic areas, close to the erupting volcano, and eventually the rare cases in which large-scale eruptions produced metre-scale ash layers in the open ocean. Moderate to very low ash-to-water ratios are more useful to examine open ocean processes within the ash fall-out area of a volcanic eruption, and coastal processes with lower ash loads towards the edge of ash fall-out areas. For wet deposition, however, the ash-to-water ratio may be highly variable.

Direct in situ measurements in nature, linking the increase of Fe within a volcanic ash fall-out area to an ash-to-seawater ratio have as yet not been performed. Unfortunately, such studies within the marine ash fall-out area of a volcanic eruption are difficult to plan and not easy to perform. Results from such projects, however, are important to verify the outcome of laboratory experiments thereby improving our understanding of the significance of volcanic ash for the marine biogeochemical iron-cycle.

4.1.4 Sieving or not sieving? Relevance for proximal and distal ash fall-out

Due to aeolian fractionation of ash particles of variable size and density, volcanic ash deposited near the volcanic source is generally coarser (e.g. in coastal areas) than that

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deposited far away (e.g. in open ocean areas). Worth noting here is that the ratio of surface area to volume increases drastically with decreasing grain size (Fig. 4), in particular for particle diameters below 200–300 μm (assuming perfect spheres) (Witham et al., 2005). Moreover, leaching studies with pristine ash from Mt. Hudson (Chile) and Hekla (Iceland) volcanoes show that the release of soluble components such as Cl, F, Ca and Na strongly increases for particle diameters below 100–200 μm (Óskarsson, 1980; Rubin et al., 1994).

It is therefore possible that fine ash particles below about 100 μm have the potential to release significantly more Fe per gram of ash than coarser particles. Partly because fine ash may carry more Fe-bearing soluble salts on their surface per mass unit but also because the solubility of solids such as glass and other silicates is also a function of grain size. Systematic studies of the Fe-release of ash as a function of grain size, however, have as yet not been performed. Some constraints though, come from repeat analysis of the 2000 Hekla sample. Frogner et al. (2001) had sieved the 2000 Hekla sample to 44–74 μm , releasing ca. 39 $\mu\text{mol Fe/g}$ ash after 45 min contact with seawater. Jones and Gislason (2008) sieved the same sample to 45–125 μm , releasing 7.1 and 8.9 $\mu\text{mol Fe/g}$ ash in natural seawater. The difference in grain size distribution may explain why the Hekla sample released more Fe in the experiments of Frogner et al. (2001). Jones and Gislason, however, also raised the aforementioned issue of the possibility of the decay of soluble salt coatings associated with the storage of the 2000 Hekla sample.

Systematic measurements of the iron-release as a function of grain size, especially distinguishing that of fine (<100–200 μm) ash, would thus be very useful to examine the impact of dry and wet deposition of volcanic ash for the marine biogeochemical iron-cycle, as a function of the distance from the volcanic source (coastal or near-coastal areas versus remote open ocean areas) and ash particle residence times in the surface ocean and cloud water.

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4.1.5 Influence of pH

Initial low pH was observed in both artificial and natural seawater in disequilibrium experiments with relatively high ash-to-seawater ratio (ca. 1:8) (Jones and Gislason, 2008; Frogner et al., 2001). The reported pH-decrease ranges from moderate 0.1–1.5 for ash samples from subduction zone volcanoes to up to $\Delta\text{pH}=5$. De Hoog et al. (2001) agitated pristine volcanic ash in ultrapure (de-ionised) water and in 1 M HNO_3 . The iron release behaviour of the same ash sample changed drastically by roughly two orders of magnitude (by a factor ranging from 30–700 with an average of 200), indicating a strong pH-influence of the iron mobilisation potential of volcanic ash. Experiments with four SZVA samples with both ultrapure water and seawater, however, do from a first glance not indicate any systematic difference in iron-release behaviour (at high ash loads) with a solute that can buffer pH and one that cannot (Jones and Gislason, 2008). In the experiment where the ash sample released more iron in de-ionised water, however, the solute also had the lowest pH (e.g. 3.5–4.0 for the Hekla ash sample), also suggesting that pH may have a substantial influence on the iron mobilisation potential of volcanic ash.

An explanation as to why pH may be an important issue for the iron-release behaviour can probably be found in the variable solubility of the salt coatings on the ash particles and the dissolution behaviour of volcanic glass. Salts found on the surface of ash particles are halogenides, oxides, sulphates and sulphides (Óskarsson, 1981). While some iron-bearing salts (e.g. halogenides and sulphates) are relatively quickly dissolved by de-ionised and slightly alkaline seawater, other salts (e.g. oxides and sulphides) may require acidic conditions to dissolve more swiftly or even to go significantly into solution at all (Smith et al., 1982). Moreover, iron is a major element in volcanic glass (contained in as much as several percentages of FeO , depending on composition). Therefore, in addition to the rapid dissolution of the soluble salt coatings, additional iron may be released through glass dissolution. The rate of glass dissolution, however, is strongly dependent on pH: Relatively slow for seawater pH of ca. 8

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and faster for an acidic pH <7, especially if fluorine and sulphate anions are present (Gislason and Oelkers, 2003; Flaathen et al., 2008; Wolff-Boenisch et al., 2004a). A temporal drop of seawater pH within an ash fall-out area, caused by the acidic components on the surface of the ash particles, may thus temporarily mobilise iron through accelerated glass dissolution. Due to the pH-buffering capacity of seawater, however, pH drop is unlikely to play a role for low ash-to-seawater ratios in the surface ocean (e.g. generally in an open ocean scenario) but can possibly play a role in areas with high ash-to-seawater ratios (e.g. in coastal areas in the vicinity of the volcanic source and even in the open ocean for very large-scale eruptions).

4.1.6 Wet and dry deposition

There is two principal ways how iron from volcanic ash may loop into the marine biogeochemical iron-cycle: 1) through offshore deposition of volcanic ash (without interaction with fog or cloud water), and subsequent dissolution primarily of soluble salt coatings in direct contact with seawater (dry deposition), 2) through dissolution of soluble salts and eventually partly of volcanic glass in contact with fog or cloud water most likely at lower pH, followed by offshore rain fall (wet deposition). Various aspects of the dry deposition process were outlined above but the mechanism of wet deposition merits some further consideration.

The role of wet deposition of volcanic ash for the surface iron-cycle is poorly constrained. Some predictions, however, can be made from what is known about glass dissolution rates and the solubility of iron. Volcanic ash typically reacts moderately to strongly acidic in contact with non-pH-buffered fresh water (Óskarsson, 1980; Jones and Gislason, 2008) and glass dissolution rates increase dramatically with decreasing pH at acidic conditions (Gislason and Oelkers, 2003). Moreover, at acidic pH, the presence of fluorine and sulphate significantly further increases the glass dissolution rates (Wolff-Boenisch et al., 2004a; Flaathen et al., 2008). Fluorine and sulphate are both contained in soluble salt coatings of volcanic ash particles (Delmelle et al., 2007). HF and SO₂ are typically released during volcanic eruptions (Oppenheimer, 2004) and

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may also find their way into cloud water. Iron usually is a major element in volcanic glass and can be released by both stoichiometric and non-stoichiometric glass dissolution. Fine (dominantly glassy) ash particles from volcanic eruptions can have relatively long residence times in the atmosphere and could therefore have a strong influence on cloud water iron-levels downwind volcanic eruptions. Worth noting is that volcanic particulate matter may act as cloud condensation nuclei. Especially fine ash particles that have coatings of hygroscopic salts are suitable to initiate the formation of water drops from atmospheric vapour (Textor et al., 2006, and references therein). Iron solubility strongly increases below pH 4 under oxidizing conditions (Kraemer, 2004). Therefore, wet deposition of volcanic ash into the surface ocean, although unconstrained up to now, may well be a common and important process for the marine biogeochemical iron-cycle.

So what iron concentrations may be reached in fog and cloud water? Numerous cloud water samples collected on Hawaii had highly variable iron concentrations ranging from <6 to 6420 nM, with a median of 32 nM (Benitez-Nelson et al., 2003). The authors linked the origin of the relatively high Fe concentrations to the activity of Hawaiian volcanoes, such as scavenging of volcanic gases while clouds pass over a degassing/erupting volcano (e.g. active Pu'u'oo) or through the formation of large aerosol clouds when lava flows enter the sea. Aerosol clouds formed due to the interaction of hot (ca. 1100–1200°C) lava with seawater were shown to have extraordinarily high concentrations of iron (ca. 250 µM) (Sansone et al., 2002), which is two to three orders of magnitude more than the iron levels in the Hawaiian cloud water samples. It is noteworthy that cloud water does not have a pH-buffer like seawater and that Hawaiian cloud water had acidic pH values between 2.6 and 5 (Benitez-Nelson et al., 2003). Interestingly, the cloud water samples with the highest Fe concentrations also had the lowest pH of around 2.7. The iron in the fog or cloud water in the aforementioned cases, is unlikely to be associated with airborne volcanic ash. The data, however, gives an idea about the Fe concentrations that may be reached in cloud water, and thus the potential role of wet deposition of volcanic ash for the marine iron-cycle. Further geochemical

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experiments with ultrapure water and volcanic ash as well as direct measurements of Fe-levels in cloud water that passed a volcanic ash plume can be expected to provide valuable new constraints.

4.1.7 Significance of Fe-complexing organic ligands

5 As outlined in more detail in Baker and Croot (2009) the solubility and thus maximum concentration of iron in seawater is closely linked to the presence of organic ligands. Organic molecules in surface ocean water are produced both directly in response to iron limitation by phytoplankton and bacteria and also by the decomposition of biomass and subsequent release of iron-containing proteins and enzymes. Some of
10 these molecules are organic chelators with a low molecular weight and a very high and specific affinity for Fe^{3+} (siderophores). More than 99% of the iron in surface ocean waters is complexed by such organic ligands that exist at sub-nanomolar levels usually in slight excess of the dissolved iron (Bruland and Lohan, 2004, and references therein). The presence and content of organic ligands can therefore strongly affect the solubility
15 and biogeochemical cycling of iron from volcanic sources in the surface ocean.

In geochemical experiments with volcanic ash and natural seawater it is common practice to filter the water through a $0.2\ \mu\text{m}$ filter and to expose it to UV-light prior to use in order to remove/destroy organic molecules and biota. Seawater samples treated this way do not contain natural marine organic ligands. The seawater used
20 for the flow-through experiments with volcanic ash was free of marine organic ligands (Frogner et al., 2001; Jones and Gislason, 2008) whereas in situ iron measurements in seawater by stripping voltammetry an electrochemically active organic ligand (e.g. TAC) was added (Olgun et al., 2009; Duggen et al., 2007; Croot and Johansson, 2000). In some of these experiments, the seawater was treated with UV-light
25 (Duggen et al., 2007), whereas more recently it was not (Olgun et al., 2009), because the TAC-ligand used is stronger and binds most of the water soluble iron. Addition of an organic ligand to a solute may also prevent loss of oxidised iron to container walls and re-precipitation to ash particle surfaces during the experiment, and therefore tend to give

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more representative analytical results.

A recent study suggests that the amount of iron that can be released from aeolian dust to seawater is strongly linked to the presence and content of natural organic ligands (Mendez et al., 2008, 2009). Thus organic ligands probably control the amount of iron that can be kept in solution, when volcanic ash fall-out swamps a surface oceanic area with bio-available iron. We are still far from a comprehensive understanding of this control, a fact highlighted in a leaching study with Mount St. Helens volcanic ash (Taylor and Lichte, 1980), which suggests that volcanic ash may inject organic ligands to experimental solutes and surface ocean water: The authors analysed the organic compounds by oxidation of the leachate followed by infrared CO₂ measurement of the released gas and found considerable amounts of organic substances in leachates of several ash samples. They argued that organic carbon on the surface of ash particles is associated with atmospheric condensation of organic compounds. These may originate from vegetation often burned during volcanic eruptions and may be sucked into the volcanic plume together with ambient air during the eruption. Low molecular weight organic compounds are also found in volcanic gases (Capaccioni and Mangani, 2001) and references therein) and may be produced in the volcanic plume or be degassing products of host rocks, sediments and soils containing organic carbon heated by ascending hot magma. The role of organic compounds of volcanic origin for the surface ocean iron-speciation and solubility has not yet been examined. Interesting to note is that some authors speculate that volcanic ash injection may cause lysis of phytoplankton in the surface ocean, leading to an enhancement of iron-complexing ligands (Randazzo et al., 2009). The role of iron-complexing organic ligands therefore merits more consideration in future studies as they play a major role for the capability of the surface ocean to keep volcanic iron in solution for biogeochemical processes.

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5 Biological response to volcanic ash fall-out in surface waters

5.1 Biological effects in fresh water systems

Biological events in lakes and rivers within ash fall-out areas of volcanic eruptions may provide constraints on the possible effects in the surface ocean. Eicher and Rounsefell (1957) observed a strong decrease in the abundance of young salmon in the four years after the eruption of the Katmai volcano in 1912 in Alaska, which was followed by a rapid recovery of the salmon stock. The recovery indicates very favourable growth conditions, which could for example result from a fertilising effect of the ash on diatom growth and thus an increased zooplankton standing stock as a food source for the salmon (Eicher and Rounsefell, 1957). In a bioassay study variable amounts of pristine volcanic ash from the 1980 Mount St. Helens eruption were added to containers with Columbia River water and juvenile salmon (Newcomb and Flagg, 1983). The results show that initial salmon mortality triggered by Mount St. Helens ash was caused by mechanical gill damage by particulate matter rather than the soluble material coating the ash. The drop in pH of the moderately hard Columbia River water was relatively minor (from 7.8 down to 7.6), thus staying well above the threshold detrimental to salmonids (pH=5.5).

Several authors show that volcanic eruptions in Kamchatka had significant influence on phytoplankton growth in lakes in Kamchatka and Alaska such as the lake Kurile (Kamchatka) after the eruption of the Alaid volcano, and the lake Asabatchye (Alaska) after the eruption of the Mount Besymjanny volcano (Kurenkov, 1966; Felitsyn and Kiryanov, 2002; Lepskaya, 1993). Kurenkov (1966) describes a strong increase of diatom biomass in 1956 in the lake Asabatchye after ash of the great eruption of the Mount Besymjanny volcano had reached the lake. Diatom abundances stayed at a distinctly higher level until 1964, 9 years after the eruption. Possibly as a result of increased diatom abundance the number of the copepod *Cyclops scutifer* also increased in winter 1960 and was 10 to 48 times higher in the period of 1960–1964 than in the 10 years before the eruption (Kurenkov, 1966). Interestingly, Kurenkov (1966) already mentioned

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that the unusual development of the algae may have been stimulated by an increased iron availability from the volcanic ash. In several lakes in the ash fall-out area of the May 1980 eruption of Mount St. Helens volcano an increase of the population of golden algae and diatoms were observed (Smith and White, 1985). Ash leachates from the 1980 Mount St. Helens eruption, however, also caused toxic effects on blue-green algae in biological experiments (McKnight et al., 1971, 1981).

In summary, these studies indicate that initial toxic effects are subsequently over-compensated by a multi-annual increase of biomass and that diatoms in lakes as well as the grazing zooplankton and fish usually benefit from volcanic ash fall-out (except for gill damage upon high ash loads).

5.2 Biological effects in the surface ocean in the Earth's history

A recent study showed that forests on western Pacific ocean islands benefit from volcanic ash fall-out (Rolett and Diamond, 2004). If plants on ocean islands do, why should phytoplankton between these islands, where the ash is deposited also, not benefit too? Key questions are if both toxic and fertilising effects in the marine environment are analogous to those identified in lakes, which species are affected and if marine iron-fertilisation with volcanic ash can be of regional or even global relevance for C-cycles and climate throughout the Earth's history. Iron-limitation and iron-fertilisation are likely to have played an important role for the marine primary productivity at least for a few millions of years but relatively little is known about how long back in the Earth's history surface ocean iron-limitation existed. So the role of volcanic ash in shaping the marine biogeochemical iron- and carbon-cycle in the past is highly uncertain. There are, however, indications on how oceanic iron-fertilisation with volcanic ash might be connected to events of marine primary productivity feed-back, among these are: 1) a termination of global warmth at the Paleocene/Eocene boundary, revealed from scientific drill core material (Bains et al., 2000), 2) the association of diatomites and volcanic ash layers in the Tertiary Danish Mo-clay formation (Duggen et al., 2007), 3) a significant increase of the relative abundance of the marine diatom *Thalassiosira oestrupii* due after the de-

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position of a ca. 10 cm ash layer ca. 450 ka ago, found in a drill core from the Southern Ocean (Kunz-Pirrung et al., 2002; Duggen et al., 2007) and 4) a correlation between volcanism and millennial climate change inferred from ice core data (Bay et al., 2004).

For the recent surface ocean, the effect of volcanic ash on the marine trace metal budget and marine phytoplankton growth is not well understood either. Geochemical experiments demonstrate an (iron-)fertilising potential of volcanic ash in several oceanic regions (Olgun et al., 2009; Jones and Gislason, 2008; Frogner et al., 2001; Duggen et al., 2007). Laboratory experiments show that marine diatoms such as *Chaetoceros dictyota* are able to use iron from volcanic ash and that they grow faster in water that has been in short-term contact with volcanic ash (ca. 20 min) compared to untreated water (Duggen et al., 2007). Further laboratory studies indicate that in general the diatom *Thalassiosira pseudonana* shows higher growth rates in waters that have been in contact with volcanic ash, while the same material has no or a strong negative effect on growth of the coccolithophoride *Emiliania huxleyi* (L. Hoffmann, unpublished data). Iron inputs through volcanic eruptions have been discussed as a possible factor controlling phytoplankton seasonality in the subarctic Pacific (Banse and English, 1999).

An anomalous oxygen pulse emanating from the Southern Hemisphere in the years following the 1991 Pinatubo eruption is consistent with an iron-fertilisation event with Pinatubo ash in the iron-limited Southern Ocean (Keeling et al., 1996; Watson, 1997; Sarmiento, 1993). It was proposed that the oxygen pulse was linked to an atmospheric CO₂-drawdown in the same years, also argued to be causally related to an iron-fertilisation effect with ash from the Pinatubo eruption (Sarmiento, 1993; Watson, 1997). The causes for the post-Pinatubo CO₂-drawdown, however, seem to be subject to ongoing discussion. It can be argued that the relative atmospheric CO₂-reduction cannot be explained by an increase in net primary production (NPP) of the terrestrial biomass, as several studies show a decrease in terrestrial NPP of up to eight years after the eruption, possibly caused by a decrease in mean summer temperatures and a shortening of the growing season (Lucht et al., 2002; Nemani et al., 2003; Awaya

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et al., 2004; Krakauer and Randerson, 2003).

For the phytoplankton bloom around erupting Soufrière Hills volcano on Montserrat mid-July 2003, as revealed by satellite data (e.g. Duggen et al., 2007), it is still unclear which phytoplankton species were involved in the bloom. Moreover, a possible increase in phytoplankton biomass in this oligotrophic oceanic area is more likely linked to fertilisation with fixed nitrogen (e.g. ammonia or nitrate) rather than iron from volcanic ash. Soufrière Hills volcano is permanently active since 1995 and in the past years the phenomenon of a seawater discolouration has been visible several times in MODIS satellite images. In the near future valuable biogeochemical data may be obtained from water samples of surface oceanic areas that are located within an ash fall-out area and show a contemporaneous discolouration. Recently, satellite data provided the first evidence for volcanic ash fall-out causing a large-scale phytoplankton bloom in an iron-limited oceanic area (Langmann et al., 2009). Such satellite techniques have only been available for about a decade and can be expected to provide more important information about the role of volcanic ash fall-out for the MPP in the near future.

6 Conclusions

Although the overall effects of volcanic eruptions on marine ecosystems are not yet comprehensively understood, do the data and evidence now available strongly suggest that volcanic ash has the potential to be an important player for the marine biogeochemical iron- cycle. Important issues to be addressed in the near future are to further constrain the Fe-release behaviour of volcanic ash on contact with seawater and cloud water; the influence of grain-size and ash-to-seawater-ratios (proximal versus distal effects) and contact-time with the solute (ash-residence-time in the euphotic zone), the relevance of ash sample degradation, the role of dry versus wet deposition, the relative importance of volcanoes in different tectonic settings, and the significance of pH-effects and organic ligands for the Fe-solubility in and Fe-keeping capacity of the surface ocean. Further biological experiments are required to evaluate as to how dif-

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ferent phytoplankton species behave in response to volcanic ash fall-out through their specific nutrient demands and tolerance levels for toxic metals. Many of such data can be obtained in the course of systematic laboratory experiments and are highly relevant for future flux estimates of Fe from volcanic ash into the surface ocean, both on a regional and global scale. In addition, direct biological, chemical and physical observations and measurements in the surface ocean during volcanic ash fall-out, combined with satellite data, can provide important new information for the surface ocean iron-cycle and the associated response of marine phytoplankton species. At this stage investigations and data suggest that the impact of volcanic activity on the surface ocean iron budget, oceanic biota and associated carbon-cycles has been underestimated so far and that volcanic ash has the potential to be as important as aeolian dust.

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References

- Awaya, Y., Kodani, E., Tanaka, K., Liu, J., Zhuang, D., and Meng, Y.: Estimation of the global net primary productivity using NOAA images and meteorological data: changes between 1988 and 1993, *Int. J. Remote Sens.*, 25, 1597–1613, 2004.
- Bains, S., Norris, R. D., Corfield, R. M., and Faul, K. L.: Termination of global warmth at the Palaeocene/Eocene boundary through productivity feedback, *Nature*, 407, 171–174, 2000.

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- Baker, A. R. and Croot, P. L.: Atmospheric and marine controls on aerosol iron solubility in seawater, *Mar. Chem.*, doi:10.1016/j.marchem.2008.09.003, in press, 2009.
- Banse, K. and English, D. C.: Comparing phytoplankton seasonality in the eastern and western subarctic Pacific and the western Bering sea, *Prog. Oceanogr.*, 43, 235–288, 1999.
- 5 Bay, R. C., Bramall, N., and Price, P. B.: Bipolar correlation of volcanism with millennial climate change, *P. Natl. Acad. Sci. USA*, 101, 6341–6345, 2004.
- Bay, R. C., Bramall, N. E., Price, P. B., Clow, G. D., Hawley, R. L., Udisti, R., and Castellano, E.: Globally synchronous ice core volcanic tracers and abrupt cooling during the last glacial period, *J. Geophys. Res.*, 111, D11108, doi:10.1029/2005JD006306, 2006.
- 10 Behrenfeld, M. J., Bale, A. J., Kolber, Z. S., Aiken, J., and Falkowski, P. G.: Confirmation of iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean, *Nature*, 383, 508–511, 1996.
- Benitez-Nelson, C. R., Vink, S. M., Carrillo, J. H., and Huebert, B. J.: Volcanically influenced iron and aluminium cloud water deposition to Hawaii, *Atmos. Environ.*, 37, 535–544, 2003.
- 15 Blain, S., Quéguiner, B., Armand, L., Belviso, S., Bombled, B., Bopp, L., Bowie, A., Brunet, C., Brussaard, C., Carlotti, F., Christaki, U., Corbière, A., Durand, I., Ebersbach, F., Fuda, J.-L., Garcia, N., Gerringa, L., Griffiths, B., Guigue, C., Guillerm, C., Jaquet, S., Jeandel, C., Laan, P., Lefèvre, D., Monaco, C. L., Malits, A., Mosseri, J., Obernosterer, I., Park, Y.-H., Picheral, M., Pondaven, P., Remenyi, T., Sandroni, V., Sarthou, G., Savoye, N., Scouarnec, L., Souhaut, M., Thuiller, D., Timmermans, K., Trull, T., Uitz, J., van Beel, P., Veldhuis, M., Vincent, D., Viollier, E., Vong, L., and Wagener, T.: Effect of natural iron fertilization on carbon sequestration on the Southern Ocean, *Nature*, 446, 1070–1074, 2007.
- 20 Boyd, P. W., Watson, A. J., Law, C. S., Abraham, E. R., Trull, T., Murdoch, R., Bakker, D. C. E., Bowie, A. R., Buesseler, K. O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M. I., Ling, R., Maldonado, M. T., McKay, R. M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., and Zeldis, J.: A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization, *Nature*, 407, 695–702, 2000.
- 25 Boyd, P. W., Law, C. S., Wong, C. S., Nojiri, Y., Tsuda, A., Levassieur, M., Takeda, S., Rivkin, R., Harrison, P. J., Strzepek, R., Gower, J., McKay, R. M., Abraham, E. R., Arychuk, M., Barwell-Clarke, J., Crawford, W., Crawford, D., Hale, M., Harada, K., Johnson, K., Kiyosawa, H., Kudo, I., Marchetti, A., Miller, W., Needoba, J., Nishioka, J., Ogawa, H., Page, J., Robert, M.,
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Saito, H., Sastri, A., Sherry, N., Soutar, T., Sutherland, N., Taira, Y., Whitney, F., Wong, S.-K. E., and Yoshimura, T.: The decline and fate of an iron-induced subarctic phytoplankton bloom, *Nature*, 428, 549–553, 2004.

Bruland, K. W. and Lohan, M. C.: Controls of trace metals in seawater, in: *The Oceans and Marine Geochemistry*, edited by: Elderfield, H., *Treatise on Geochemistry*, Elsevier Pergamon, Amsterdam-Boston-Heidelberg-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo, 23–47, 2004.

Capaccioni, B. and Mangani, F.: Monitoring of active but quiescent volcanoes using light hydrocarbon distribution in volcanic gases: the results of 4 years of discontinuous monitoring in the Campi Flegrei (Italy), *Earth Planet. Sc. Lett.*, 188, 543–555, 2001.

Christenson, B. W.: Geochemistry of fluids associated with the 1995–1996 eruption of Mt. Ruapehu, New Zealand: signatures and processes in the magmatic-hydrothermal system, *J. Volcanol. Geoth. Res.*, 97, 1–30, 2000.

Cimino, G. and Toscano, G.: Dissolution of trace metals from lava ash: influence on the composition of rainwater in the Mount Etna volcanic area, *Environ. Pollut.*, 99, 389–393, 1998.

Coale, K. H., Johnson, K. S., Fitzwater, S. E., Gordon, R. M., Tanner, S. J., Chavez, F. P., Ferioli, L., Sakamoto, C., Rogers, P., Millero, F., Steinberg, P., Nightingale, P., Cooper, D., Cochlan, W. P., Landry, M. R., Constantiniou, J., Rollwagen, G., Trasvina, A., and Kudela, R.: A massive phytoplankton bloom induced by an ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean, *Nature*, 383, 495–501, 1996.

Coale, K. H., Johnson, K. S., Chavez, F. P., Buesseler, K. O., Barber, R. T., Brzezinski, M. A., Cochlan, W. P., Millero, F., Falkowski, P. G., Bauer, J. E., Wanninkhof, R. H., Kudela, R. M., Altabet, A. M., Hales, B. E., Takahashi, T., Landry, M. R., Bidigare, R. R., Wang, X., Chase, Z., Strutton, P. G., Friederich, G. E., Gorbunov, M. Y., Lance, V. P., Hilting, A. K., Hiscock, W. T., Sullivan, K. F., Tanner, S. J., Gordon, R. M., Hunter, C. N., Elrod, V. A., Fitzwater, S. E., Jones, J. L., Tozzi, S., Koblizek, M., Roberts, A. E., Herndon, J., Brewster, J., Ladizinsky, N., Smith, G., Cooper, D., Timothy, D., Brown, S. L., Selph, K. E., Sheridan, C. C., Twining, B. S., and Johnson, Z. I.: Southern Ocean iron enrichment experiment: carbon cycling in high- and low-Si waters, *Science*, 304, 408–414, 2004.

Cooper, D. J., Watson, A. J., and Nightingale, P. D.: Large decrease in ocean-surface CO₂ fugacity in response to in situ iron fertilization, *Nature*, 383, 511–513, 1996.

Croot, P. and Johansson, M.: Determination of iron speciation by cathodic stripping voltammetry in seawater using the competing ligand 2-(2-thiazolylazo)-*p*-creosol (TAC), *Electroanaly-*

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sis, 12, 565–576, 2000.

De Baar, J. W. O. and De Jong, J. T. M.: Distributions, Sources and Sinks of Iron in Seawater, in: Biogeochemistry of iron in seawater, edited by: Turner, D. R. and Hunter, K., Wiley, Chichester, 124–233, 2001.

5 de Hoog, J. C. M., Koetsier, G. W., Bronto, S., Sriwana, T., and van Bergen, M. J.: Sulfur and chlorine degassing from primitive arc magmas: temporal changes during the 1982–1963 eruptions of Galunggung (West Java, Indonesia), *J. Volcanol. Geoth. Res.*, 108, 55–83, 2001.

10 Delmelle, P., Lambert, M., Dufrene, Y., Gerin, P., and Óskarsson, N.: Gas/aerosol-ash interaction in volcanic plumes: new insights from surface analyses of fine ash particles, *Earth Planet. Sc. Lett.*, 259, 159–170, 2007.

Duggen, S., Croot, P., Schacht, U., and Hoffmann, L.: Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: evidence from biogeochemical experiments and satellite data, *Geophys. Res. Lett.*, 34, 5, doi:10.1029/2006GL027522, 2007.

15 Eicher, G. J. and Rounsefell, G. A.: Effects of lake fertilization by volcanic activity on abundance of salmon, *Limnol. Oceanogr.*, 2, 70–76, 1957.

Felitsyn, S. B. and Kirianov, V. Y.: Mobility of phosphorous during weathering of volcanic ashes, *Lithol. Miner. Resour.*, 37, 275–278, 2002.

20 Fisher, R. V. and Schmincke, H.-U.: *Pyroclastic Rocks*, Springer-Verlag, Berlin-Heidelberg-New York-Tokyo, 472 pp., 1984.

Flaathen, T. K., Oelkers, E. H., and Gislason, S. R.: The effect of aqueous sulphate on basaltic glass dissolution rates, *Mineral. Mag.*, 72, 39–41, 2008.

Frogner Kockum, P. C.: A diverse ecosystem response to volcanic aerosols, *Chem. Geol.*, 231, 57–66, 2006.

25 Frogner, P., Gislason, S. R., and Oskarsson, N.: Fertilization potential of volcanic ash in ocean surface waters (Goldschmidt Conference 2000, Oxford), *J. Conf. Abs.*, 5, 415, 2000.

Frogner, P., Gíslason, S. R., and Óskarsson, N.: Fertilizing potential of volcanic ash in ocean surface water, *Geology*, 29, 487–490, 2001.

30 Fruchter, J. S., Robertson, D. E., Evans, J. C., Olsen, K. B., Lepel, E. A., Laul, J. C., Abel, K. H., Sanders, R. W., Jackson, P. O., Wogman, N. S., Perkins, R. W., van Tuyl, H. H., Beauchamp, R. H., Shade, J. W., Daniel, J. L., Erikson, R. L., Sehmel, G. A., Lee, R. N., Robinson, A. V., Moss, O. R., Briant, J. K., and Cannon, W. C.: Mount St. Helens ash from the 18 May 1980 eruption: chemical, physical, mineralogical, and biological properties, *Sci-*

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ence, 209, 1116–1125, 1980.

Gislason, S. R. and Oelkers, E. H.: Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature, *Geochim. Cosmochim. Ac.*, 67, 3817–3832, 2003.

5 Gran, H. H.: On the conditions for the production of plankton in the sea, *Rapp. Proc. Verb. Cons. Int. Explor. Mer.*, 75, 37–46, 1931.

Harvey, H. W.: The supply of iron to diatoms, *J. Mar. Biol. Assoc.*, XXII, 205–219, 1937.

Jones, M. T. and Gislason, S. R.: Rapid releases of metal salts and nutrients following the deposition of volcanic ash into aqueous environments, *Geochim. Cosmochim. Ac.*, 72, 3661–3680, 2008.

10 Keeling, R. F., Piper, S. C., and Heimann, M.: Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration, *Nature*, 381, 218–221, 1996.

Kraemer, S. M.: Iron oxide dissolution and solubility in the presence of siderophores, *Aquat. Sci.*, 66, 3–18, 2004.

15 Krakauer, N. Y. and Randerson, J. T.: Do volcanic eruptions enhance or diminish net primary production? Evidence from tree rings, *Global Biogeochem. Cycles*, 17, 002003, doi:10.1029/2003GB002076, 2003.

Kunz-Pirrung, M., Gersonde, R., and Hodell, D. A.: Mid-Brunhes century-scale diatom sea surface temperature and sea ice records from the Atlantic sector of the Southern Ocean (ODP Leg 177, sites 1093, 1094 and core PS2089-2), *Palaeogeogr. Palaeoecol.*, 182, 305–328, 2002.

20 Kurenkov, I. I.: The influence of volcanic ashfall on biological processes in a lake, *Limnol. Oceanogr.*, 11, 426–429, 1966.

Kutterolf, S., Freundt, A., and Peréz, W.: Pacific offshore record of plinian arc volcanism in Central America: 2. Tephra volumes and erupted masses, *Geochem. Geophys. Geosy.*, 9, 1–19, 2008.

Langmann, B., Zaksek, K., Hort, M., and Duggen, S.: Natural large-scale surface ocean iron-fertilisation by volcanic ash, *Geophys. Res. Lett.*, in review, 2009.

Larsson, W.: Vulkanische Asche vom Ausbruch des chilenischen Vulkans Quizapu (1932) in Argentinien gesammelt. Eine Studie über äolische Differentiation, *Geol. Inst. Upsala Bull.*, 26, 27–52, 1937.

30 Lepskaya, E. V.: Influence of Ash from the Alaid Volcano on Phytoplankton of Lake Kurile (Southern Kamchatka), in: *Issledovaniya biologii i dinamiki chislennosti promyslovykh ryb*

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Kamchatskogo shel'fa (The Study of Biology and Dynamics of Commercial Fish Population on the Kamchatka Shelf), 2, Min-vo Rybn, Khoz-va, Petropavlovsk-Kamchatskii, 21–24, 1993.

Lucht, W., Prentice, I. C., Myneni, R. B., Sitch, S., Friedlingsstein, P., Cramer, W., Bousquet, P., Buermann, W., and Smith, B.: Climatic control of the high-latitude vegetation greening trend and Pinatubo effect, *Science*, 296, 1687–1689, 2002.

Martin, J. H. and Fitzwater, S. E.: Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic, *Nature*, 331, 341–343, 1988.

Martin, J. H., Gordon, R. M., and Fitzwater, S. E.: Iron in Antarctic waters, *Nature*, 345, 156–158, 1990.

McKnight, D. M., Feder, G. L., and Stiles, E. A.: Effects on a blue-green alga of leachates of ash from the May 18 eruption, in: *The 1980 Eruptions of Mount St. Helens*, edited by: Lipman, P. W. and Mullineaux, D. R., USGS Professional Paper, Washington, 733–741, 1971.

McKnight, D. M., Feder, G. L., and Stiles, E. A.: Toxicity of volcanic-ash leachate to a blue-green alga: results of a preliminary bioassay experiment, *Envir. Sci. Tech. Lib.*, 15, 362–364, 1981.

Mendez, J., Guieu, C., and Adkins, J.: Atmospheric input of manganese and iron to the ocean: seawater dissolution experiments with Saharan and North American dusts, *Mar. Chem.*, in press, 2009.

Middleton, G. V., Church, M. J., Coniglio, M., et al.: *Encyclopedia of Sediments and Sedimentary Rocks*, Springer, Boston, 2003.

Mills, M. M., Ridame, C., Davey, M., La Roche, J., and Geider, R.: Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature*, 429, 292–294, 2004.

Morel, F. M. M., Milligan, A. J., and Saito, M. A.: Marine bioinorganic chemistry: The role of trace metals in the oceanic cycles of major nutrients, in: *The Oceans and Marine Geochemistry*, edited by: Elderfield, H., Treatise on Geochemistry, Elsevier Pergamon, Amsterdam-Boston-Heidelberg-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo, 113–143, 2004.

Moune, S., Gauthier, P.-J., Gislason, S. R., and Sigmarsson, O.: Trace element degassing and enrichment in the eruptive plume of the 2000 eruption of Hekla volcano, Iceland, *Geochim. Cosmochim. Ac.*, 70, 461–479, 2006.

Nehring, N. L. and Johnston, D. A.: Use of ash leachates to monitor gas emissions, in: *The 1980 Eruptions of Mount St. Helens*, edited by: Lipman, P. W. and Mullineaux, D. R., USGS

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Professional Paper, Washington, 251–254, 1981.

Nemani, R. R., Keeling, C. D., Hashimoto, H., Jolly, W. M., Piper, S. C., Tucker, C. J., Myrneni, R. B., and Running, S. W.: Climate-driven increases in global terrestrial net primary production from 1982–1999, *Science*, 300, 1560–1563, 2003.

5 Newcomb, T. W. and Flagg, T. A.: Some effects of Mount St. Helens volcanic ash on juvenile samlon smolts, *Mar. Fish. Rev.*, 45, 8–12, 1983.

Nielsen, S. H. H., Hodell, D. A., Kamenov, G., Guilderson, T., and Perfit, M. R.: Origin and significance of ice-rafted detritus in the Atlantic sector of the Southern Ocean, *Geochem. Geophys. Geosy.*, 8, 1–23, 2007.

10 Olgun, N., Duggen, S., Croot, P., Dietze, H., Schacht, U., Óskarsson, N., Siebe, C., and Auer, A.: Surface ocean iron fertilization: the role of subduction zones and hotspot volcanic ash and fluxes into the Pacific Ocean, *Global Biogeochem. Cy.*, in preparation, 2009.

Oppenheimer, C.: Limited global change due to the largest known Quaternary eruption, Toba \approx 74 kyr BP?, *Quaternary Sci. Rev.*, 21, 1593–1609, 2002.

15 Oppenheimer, C.: Volcanic Degassing, in: *The Crust*, edited by: Rudnick, R. L., Treatise on Geochemistry, Elsevier Pergamon, Amsterdam-Boston-Heidelberg-London-New York-Oxford-Paris-San Diego-San Francisco-Singapore-Sydney-Tokyo, 123–166, 2004.

Óskarsson, N.: The interaction between volcanic gases and tephra: flourine adhering to tephra of the 1970 Hekla eruption, *J. Volcanol. Geoth. Res.*, 8, 251–266, 1980.

20 Óskarsson, N.: The chemistry of Icelandic lava incrustations and the latest stages of degassing, *J. Volcanol. Geoth. Res.*, 10, 93–111, 1981.

Parekh, P., Follows, M. J., and Boyle, E. A.: Decoupling of iron and phosphate in the global ocean, *Global Biogeochem. Cycles*, 19, 1–16, 2005.

25 Pedersen, G. K. and Surlyk, F.: Dish structures in Eocene volcanic ash layers, Denmark, *Sedimentology*, 24, 581–590, 1977.

Randazzo, L. A., Censi, P., Saiano, F., Zuddas, P., Aricò, P., and Mazzola, S.: Trace elements release from volcanic ash to seawater. Natural concentrations in Central Mediterranean Sea, European Geosciences Union Meeting, Vienna, 2009,

30 Rea, D. K., Scholl, D. W., and Allan, J. F.: Proceedings of the Ocean Drilling Program 145, Scientific Results, 1995.

Rolett, B. and Diamond, J.: Environmental predictors of pre-European deforestation on Pacific islands, *Nature*, 431, 443–446, 2004.

Rubin, C. H., Noji, E. K., Seligman, P. J., Holtz, J. L., Grande, J., and Vittani, F.: Evaluating

- a flourosis hazard after a volcanic eruption, Arch. Environ. Health, 49, 395–401, 1994.
- Sansone, F. J., Benitez-Nielson, C. R., DeCarlo, E. H., Resing, J. A., Vink, S. M., Heath, J. A., and Huebert, B. J.: Geochemistry of atmospheric aerosols generated from lava-seawater interactions, Geophys. Res. Lett., 29, 1–4, 2002.
- 5 Sarmiento, J. L.: Atmospheric CO₂ stalled, Nature, 365, 697–698, 1993.
- Schmincke, H.-U.: Volcanism, Springer-Verlag, Berlin Heidelberg New York, 324 pp., 2004.
- Smith, D. B., Zielinski, R. A., and Rose, W. I.: Leachability of uranium and other elements from freshly erupted volcanic ash, J. Volcanol. Geoth. Res., 13, 1–30, 1982.
- 10 Smith, D. B., Zielinski, R. A., Taylor, H. E., and Sawyer, M. B.: Leaching characteristics of ash from the May 18, 1980, eruption of Mount St. Helens volcano, Washington, B. Volcanol., 46, 103–124, 1983.
- Smith, M. A. and White, M.: Observations on lakes near Mount St. Helens: phytoplankton, J. Arch. Hydrobiol., 104, 345–363, 1985.
- Spirakis, C. S.: Iron fertilization with volcanic ash?, Eos (Trans. Am. Geophys. Union), Nov. 19, 2, 1991.
- 15 Straub, S. M. and Schmincke, H.-U.: Evaluating the tephra input into Pacific Ocean sediments: distribution in space and time, Geol. Rundsch., 87, 461–476, 1998.
- Taylor, H. E. and Lichte, F. E.: Chemical composition of Mount St. Helens volcanic ash, Geophys. Res. Lett., 7, 949–952, 1980.
- 20 Textor, C., Graf, H. F., Herzog, M., Oberhuber, J. M., Rose, W. I., and Ernst, G. G. J.: Volcanic particle aggregation in explosive eruption columns. Part I: Parameterization of the microphysics of hydrometeors and ash, J. Volcanol. Geoth. Res., 150, 359–377, 2006.
- Uematsu, M., Toratani, M., M., K., Narita, Y., Senga, Y., and Kimoto, T.: Enhancement of primary productivity in the western North Pacific caused by the eruption of the Miyake-jima volcano, Geophys. Res. Lett., 31, 1–4, 2004.
- 25 Walker, G. P. L. and Craosdale, R.: Characteristics of some basaltic pyroclastics, B. Volcanol., 35, 303–317, 1972.
- Watson, A. J.: Volcanic Fe, CO₂, ocean productivity and climate, Nature, 385, 587–588, 1997.
- Wells, M. L.: The level of iron enrichment required to initiate diatom blooms in HNLC waters, Mar. Chem., 82, 101–114, 2003.
- 30 Wiesner, M. G., Wetzell, A., Catane, S. G., Listanco, E. L., and Mirabueno, H. T.: Grain size, areal thickness distribution and controls on sedimentation of the 1991 Mount Pinatubo tephra layer in the South China Sea, B. Volcanol., 66, 226–242, 2004.

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Witham, C. S., Oppenheimer, C., and Horwell, C. J.: Volcanic ash-leachates: a review and recommendations for sampling methods, *J. Volcanol. Geoth. Res.*, 141, 299–326, 2005.

Wolff-Boenisch, D., Gislason, S. R., and Oelkers, E. H.: The effect of fluoride on the dissolution rates of natural glasses at pH 4 and 25°C, *Geochim. Cosmochim. Ac.*, 68, 4571–4582, 2004a.

Wolff-Boenisch, D., Gislason, S. R., Oelkers, E. H., and Putnis, C. V.: The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74°C, *Geochim. Cosmochim. Ac.*, 68, 4843–4858, 2004b.

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6, 6441–6489, 2009

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Table 1. Overview of the iron-release behaviour of pristine (unhydrated or dry) volcanic ash from geochemical (leaching) experiments in the literature.

Reference	Method	Duration of the experiment	Number and type of ash sample(s)	Particle size fraction	Ash/solute ratio (g/ml)	Solute	Fe-release (nmol Fe/g ash)
Fruchter et al. (1980)	Agitation	1 h (10 min stirring followed by resting)	9 samples from 1 SZ volcano (Mount St. Helens, 1980)	Unsieved	1:10 (quantities not mentioned only the ratio!)	Distilled water	0.9–315.2
Taylor and Lichte (1980)	Agitation	4 h in column	4 samples from 1 SZ volcano (Mount St. Helens, 1980)	Unsieved	1:0.58 (172 g ash and 100 ml solute)	Deionised water	0.2–0.4
Nehring and Johnston (1981)	Agitation	1 h stirring	4 samples from 1 SZ volcano (Mount St. Helens, 1980)	Unsieved	1:2.5 (20 g ash, 50 ml solute)	Triply distilled water	0.2–13.9
McKnight et al. (1981)	Flow-through columns	9 h, 12 h, 14 h in columns followed by elution	2 samples from 1 SZ volcano (Mount St. Helens, 1980)	Unsieved	1:1.25 1:0.87 (15–20 g ash, 50–70 ml solute)	WC medium	<0.2
Smith et al. (1982)	Agitation	1 h shaking followed by resting overnight	30 samples from 3 SZ volcanoes (Fuego 1974 $n=13$, Fuego 1973, $n=5$, Pacaya 1974, $n=7$, Santiaguita 1967, $n=1$, Santiaguita 1976; 1975, $n=4$)	850–106 μm and 106 μm after crushing	1:4 (5 g ash, 20 ml solute)	Distilled-deionized water HCl solution (pH: 3.5–4.0) 0.05 M sodium carbonate and bicarbonate (pH=9.9)	2.0–401.1 0.7–458.4 12.9–71.6

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Table 1. Continued.

Reference	Method	Duration of the experiment	Number and type of ash sample(s)	Particle size fraction	Ash/solute ratio (g/ml)	Solute	Fe-release (nmol Fe/g ash)
Smith et al. (1983)	Agitation	1 h agitation followed by resting overnight (1 week for the carbonate solution)	19 samples from 1 SZ volcano (Mount St. Helens, 1980)	Unsieved	1:4 (5 g ash, 20 ml solute)	Distilled-deionized water	<0.1–8.6
						HCl solution (pH: 3.5–4.0)	<0.1–93.1
						0.05 M sodium carbonate and bicarbonate (ph: 9.9)	5.6–34.4
Cimino and Toscano (1998)	Agitation	24 h	Fresh lava ash (Mount Etna, 1996)	0.1–0.3 mm	1:10 1:33 1:500 1:1000 (1, 2, 30, 100 g ash, 1 L solute)	Doubly distilled water	<0.1–268.6
Christenson (2000)	Agitation	15 min agitation followed by resting overnight	22 samples from 1 SZ volcano (Mount Ruapehu 1995, 1996)	Unsieved	1:10 (10 g ash, 100 g water)	Distilled-deionised water, then heated to 60°C	17.9–1504
de Hoog et al. (2001)	Agitation	4 h	8 samples from 1 SZ volcano (Galunggung, 1982)	Unsieved	1:80 (0.5 g ash, 40 ml solute)	DI water	1000–23000
						1 M HNO ₃	200 000–1 500 000

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Table 1. Continued.

Reference	Method	Duration of the experiment	Number and type of ash sample(s)	Particle size fraction	Ash/solute ratio (g/ml)	Solute	Fe-release (nmol Fe/g ash)
Frogner et al. (2001)	Flow-through reactor	Solute sampled every ca. 45 min. Total duration 8 h.	1 sample from 1 HS volcano (Hekla, 2000)	45–74 μm	1:8 (5 g ash, 40 ml solute)	Artificial seawater	39,000 within 45 min
						North Atlantic seawater	37,000 within 45 min
Duggen et al. (2007)	In situ by stripping voltammetry	Up to 1 h with measurements	5 samples from 3 SZ volcanoes (Sakura-Jima 1986, 1987, 1999 $n=3$; Mount Spurr 1991 $n=1$; Arenal 1993 $n=1$)	Unsieved	1:400 (50 mg ash, 20 ml seawater)	Antarctic seawater	18.4–72.4 (after 1 h)
Jones and Gislason (2008)	Flow-through reactor	One experiment with 15 h	$n=1$ Arenal	45–125 μm	1:8 (5 g ash, 40 ml solute)	De-ionized (DI) water	135.4 (after 15 h)
		Solute sampled every ca. 45 min. Total duration 8 h (DI water) or 24 h (seawater).	3 samples from 3 SZ volcanoes and 1 sample from 1 HS volcano (Galeras 2005 $n=1$; Montserrat 2003 $n=1$; Santiaguito 1998 $n=1$; Hekla 2000 $n=1$)			Atlantic seawater	10–120 (for SZVA) 10,900 (for HSVA) 20–100 (for SZVA) 7 100 for HSVA
						Southern Ocean seawater	10–40 (for SZVA) 8 900 (for HSVA)

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Reference	Method	Duration of the experiment	Number and type of ash sample(s)	Particle size fraction	Ash/solute ratio (g/ml)	Solute	Fe-release (nmol Fe/g ash)
Olgun et al. (2009)	In situ by stripping voltametry	Up to 1 h with measurements every several minutes	32 samples from 8 SZ volcanoes and 4 samples from 2 HS volcanoes (Sakura-Jima 1986, 1987, 1999, 2007 <i>n</i> =4; Arenal 1992, 1993, 2003, 2004 <i>n</i> =4; Mount Spurr 1992 <i>n</i> =1; Turrialba 1864 <i>n</i> =1; Rabaul-Tavurvur 2002 <i>n</i> =2; Popocatepetl 1998, 2000, 2001, 2003 <i>n</i> =8; Karymsky 2005 <i>n</i> =10; Chaïten 2008 <i>n</i> =2; Hekla 1947, 1970, 1980 <i>n</i> =3; Pu'u'oo 2005 <i>n</i> =1)	Unsieved	1:400 (50 mg ash, 20 ml seawater)	Atlantic seawater	41.8–318.8 (for SZVA) 34.8–107.4 (for HSVA)

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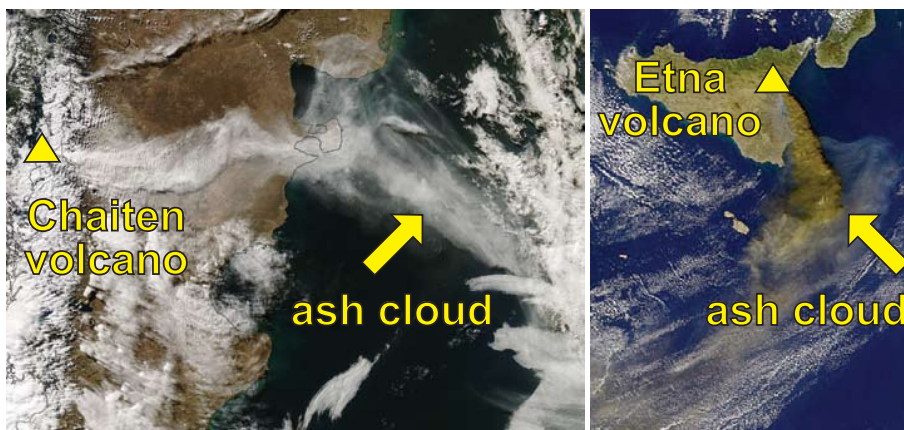


Fig. 1. NASA satellite images of eruptions of the volcanoes Chaiten in Southern Chile in 2008 and Etna on Sicily in 2002. The pictures illustrate seaward transport and offshore deposition of volcanic ash (eastward to the Atlantic sector of the Southern Ocean for Chaiten and southward into the Central Mediterranean Sea for Etna). Depending on composition the colour of the volcanic ash visible from space ranges from white (e.g. Chaiten) to brown (e.g. Etna).

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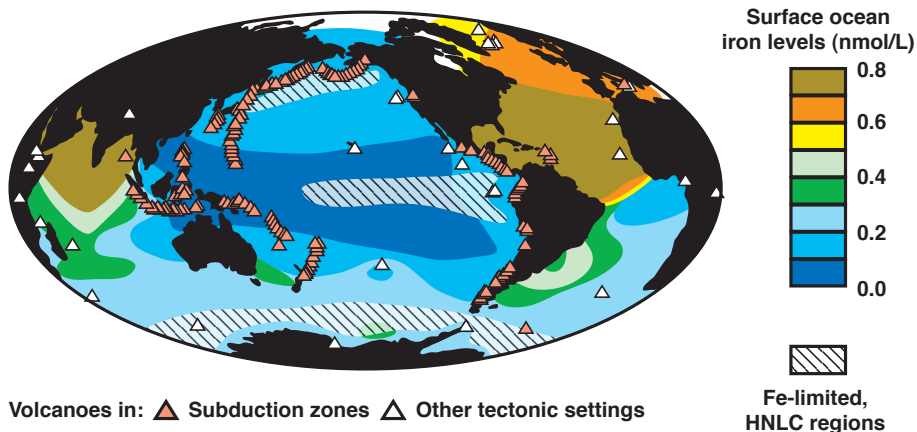


Fig. 2. World map showing surface ocean iron-concentrations, locations of iron-limited (HNLC) regions and subaerially and historically active volcanoes in subduction zones and other tectonic settings. Data sources are: surface ocean iron-concentrations (Parekh et al., 2005), location of volcanoes (Sigurdsson et al., 2000).

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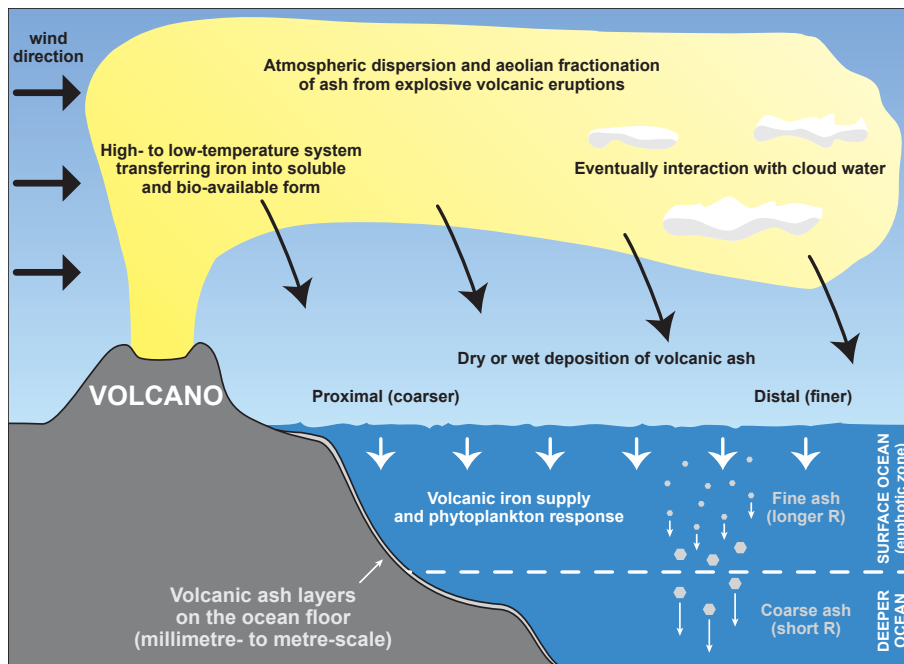


Fig. 3. Sketch displaying the possible effects of major volcanic eruptions on the marine environment, with focus on the surface ocean (R – surface ocean residence time).

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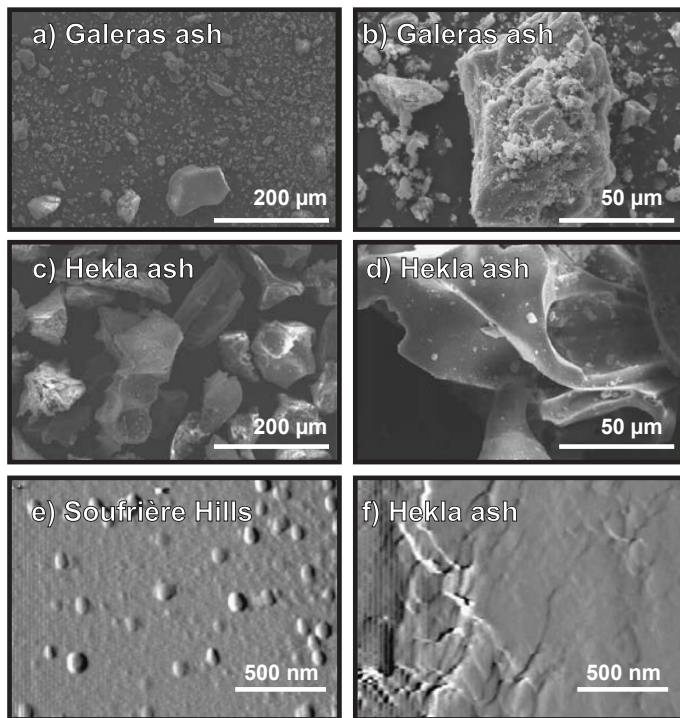


Fig. 4. Examples of volcanic ash and its physical properties such as grain size distribution, shape and surface topography of the particles. The ash displayed at different magnifications is from the 2005 eruption of Galeras volcano in Columbia (**a,b**) and 2000 eruption of Hekla volcano in Iceland (**c,d**). Panels e and f show AFM images showing nodules and smooth terraces forming soluble salt coatings at the surface of ash particles from eruptions of Soufrière Hills volcano 1999 (Montserrat) (**e**) and Hekla volcano 1970 (**f**). Data sources are: scanning electron microscope (SEM) images (Jones and Gislason, 2008), atomic force microscope (AFM) images (Delmelle et al., 2007).

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