

Review Article

On the Role of Climate Forcing by Volcanic Sulphate and Volcanic Ash

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There is overall agreement that volcanic sulphate aerosols in the stratosphere can reduce solar radiation reaching the earth's surface for years, thereby reducing surface temperatures, affecting global circulation patterns and generally the global climate system. However, the response of the climate system after large volcanic eruptions is not fully understood and global climate models have difficulties to reproduce the observed variability of the earth system after large volcanic eruptions until now. For geological timescales, it has been suggested that, in addition to the stratospheric climate forcing by volcanic sulphate aerosols, volcanic ash affects climate by modifying the global carbon cycle through iron fertilising the surface ocean and stimulating phytoplankton growth. This process has recently also been observed after the eruption of the volcano Kasatochi on the Aleutian Islands in summer 2008. To trigger future research on the effect of volcanic ash on the climate system via ocean iron fertilisation, this review paper describes the formation processes and atmospheric life cycles of volcanic sulphate and volcanic ash, contrasts their impact on climate, and emphasises current limitations in our understanding.

1. Introduction

Volcanic emissions are an important source of atmospheric gases, aerosols, and ash [1–3]. Volcanic ash is formed by fragmentation processes of the magma and the surrounding rock material within volcanic vents [1, 4]. Volcanic gas emissions from the magma consist primarily of H₂O, followed by CO₂, SO₂, H₂S, HCl, HF, and other compounds [5]. Secondary products like volcanic sulphate aerosols result from high- and low-temperature chemical transformation processes in the conduit, the volcanic plume, and cloud [6–9].

When volcanic emissions are released into the free troposphere or stratosphere [1, 6], they are transported by the prevailing winds and modified photochemically and microphysically before being removed from the atmosphere by gravitational settling and wet deposition. Post-eruptive remobilisation of volcanic ash from its deposits represents another source for volcanic ash in the atmosphere [10–15].

Since the volcanic eruptions of El Chichón in 1982 and Mt. Pinatubo in 1991, the importance of volcanic ash for climate has been considered negligible, whereas the climate forcing of volcanic sulphate received increasing attention [16].

Today, it is widely accepted in the climate and volcanological research communities that the major climate forcing effect following explosive volcanic eruptions is through their emission of sulphur species into the stratosphere. These are mainly in the form of SO₂ [17–19] and sometimes also H₂S [20–23]. They are oxidised to sulphate aerosols within weeks. Volcanic sulphate aerosols in the stratosphere can reduce solar radiation reaching the earth's surface for years, thereby reducing surface temperatures and affecting global circulation patterns and generally the global climate system [6]. Several previous reviews discuss the effects of volcanoes on climate, for example, references [24–32]. Except [24], all of these studies focus on the climatic effect of volcanic sulphate aerosols. According to [6, 31], volcanic ash and tephra (tephra definition: fragmental matter of any size and composition created during a volcanic eruption; [2]) have very small climatic impacts, which are restricted to the residence time of these particles in the atmosphere. In contrast to volcanic gases and aerosols, volcanic ash is removed from the atmosphere more rapidly after an eruption. Only submicron volcanic ash particles have been observed for several months in the lower stratosphere following major volcanic eruptions [33, 34].

During a period of up to few weeks the huge atmospheric load of volcanic ash close to the source region may affect the amplitude of the diurnal cycle of surface air temperature.

However, [6, 30, 31] neglect the impact that volcanic ash has on the biogeochemistry of the ocean; volcanic ash may activate the “biological pump,” a process that converts CO_2 to organic carbon and allows organic matter particles to sink to the deep ocean, thereby reducing atmospheric CO_2 . Recent work showed that airborne material from volcanic eruptions, in particular volcanic ash, modifies the biogeochemical processes in the surface ocean [35–39], thereby directly affecting climate. References [40, 41] first speculated about oceanic iron-induced biogeochemical processes by volcanic ash after the 1991 Pinatubo eruption. However, these processes remained largely unconsidered in the volcano-climate research community until the eruption of Kasatochi volcano on the Aleutian Islands in August 2008. After this eruption, favourable atmospheric and oceanic conditions in the NE Pacific enabled the formation of an immense phytoplankton bloom, observed over a wide area by satellite instruments [36], *in situ* measurements [42, 43], and modelling studies [44]. This event was the first to confirm that volcanic ash can successfully fertilise the surface ocean, potentially having an effect on climate. Volcanic ash can therefore play a role similar to mineral dust, which is commonly assumed to dominate external iron supply to the open ocean [45].

In this review climatic effects of volcanic ash versus those of volcanic sulphate are discussed and new light is shed on the effects of volcanic eruptions on climate (Figure 1). The review aims to stimulate new discussions and joint and interdisciplinary research projects involving research communities specialised in ocean biogeochemistry and biology, volcanology, geochemistry, meteorology, atmospheric chemistry, and climate. An improved understanding of natural causes of climate change—including volcanic eruptions—is indispensable when interpreting natural climate variability, even in the era of anthropogenic climate change. The following Sections 2 and 3 describe the fate of volcanic ash and sulphate chronologically from the formation processes over the atmospheric burden to postatmospheric deposition. Climate forcing is presented in Section 4. Section 5 provides an outlook on future research needs.

2. Formation Processes and Chemical and Physical Characteristics

2.1. Frequency of Volcanic Eruptions. Annually, 50–70 volcanic eruptions lasting from hours to years occur worldwide with about 20 volcanoes erupting at any defined date [46]. Volcanic eruptions with a Volcanic Explosivity Index (VEI, relative measure of the explosiveness of volcanic eruption; [18]) smaller than 4 are most numerous. Volcanic ash emission into the troposphere from these small eruptions is estimated to 20 Tg/yr [47]. However, before the satellite era, our knowledge of volcanic eruptions with $\text{VEI} \leq 4$ is limited because of restricted observation capabilities of remote volcanic eruptions. Nevertheless, these ash emissions are only of local interest due to rapid deposition out of

the atmosphere. Reference [48] summarises ash emissions from major volcanic eruptions since 1900 with $\text{VEI} \geq 4$ and with a tephra release ranging from 0.1 to 100 km³. During such volcanic eruptions, volcanic ash can undergo long-range transport and submicron ash particles may survive for months in the atmosphere [33, 34].

Sulphur containing gases contribute typically 2–35% to the volcanic gas emissions [31] with values of 14–21 Tg/yr for SO_2 [21, 49] and 1–37 Tg/yr for H_2S [21]. Although global sulphur emissions from volcanoes make up only ~14% of the total natural and anthropogenic sulphur emissions [49], they have a much larger relative contribution to radiative and climate effects (see Section 4). As volcanic emissions are mainly released above the atmospheric boundary layer due to the height of volcano summits, they have longer lifetimes than anthropogenically released sulphur compounds (see Section 3).

2.2. Chemical and Mechanical Processes below the Earth Surface. The erupting magma mainly determines the chemical composition of volcanic ash with a silica content between about 45 and 75 wt-% [50] and melting temperatures between ~650 and ~1200°C. Reference [51] analysed volcanic ash from the 1989 Redoubt eruption (Alaska) and found that the ash consisted of 70 wt-% of silica glass and 30 wt-% of minerals. Volcanic ash minerals like feldspar, olivine, pyroxene, hornblende, biotite, magnetite, and ilmenite [52] have their origin in a sequential crystallisation process, which is driven by cooling and decompression during the rise of the magma through the earth’s crust.

When magma containing dissolved volatiles like H_2O , CO_2 , SO_2 , H_2S , HCl , HF , and other compounds [5] rises through the earth’s mantle and crust into the conduit, volatiles get separated from the magma in form of gas bubbles eventually triggering an explosive eruption [1]. During explosive volcanic eruptions with rhyolitic magma, usually abundant fragmentation of magma is observed. However, plinian (highly explosive) volcanic eruptions occur also at volcanoes with andesitic magma composition, for example, at Shiveluch, Kamchatka [53].

There is ongoing discussion about the differing amount of volcanic SO_2 emissions from explosive volcanic eruptions as measured by petrological methods and remote sensing [54–56]. The expression of “excess sulphur” was introduced to describe the much lower dissolved sulphur concentration in magmas (by 1 to 2 orders of magnitude) in comparison to the total mass of SO_2 released during an eruption as measured by remote sensing techniques [56]. Petrological data provide a minimum estimate of the erupted sulphur [57] because the melt droplets included in the magma, which are analysed to estimate the pre-eruptive sulphur content, do not account for any eruptive phase chemical conversion. Excess eruptive sulphur is observed particularly during explosive eruptions of intermediate and silicic magma in subduction zone settings [58, 59] rather than for basaltic eruptions from divergent plate boundaries and hot spots. Reference [60] proposed that arc magmas coexist with a substantial vapour phase in crustal storage regions. According to [61, 62], shallow

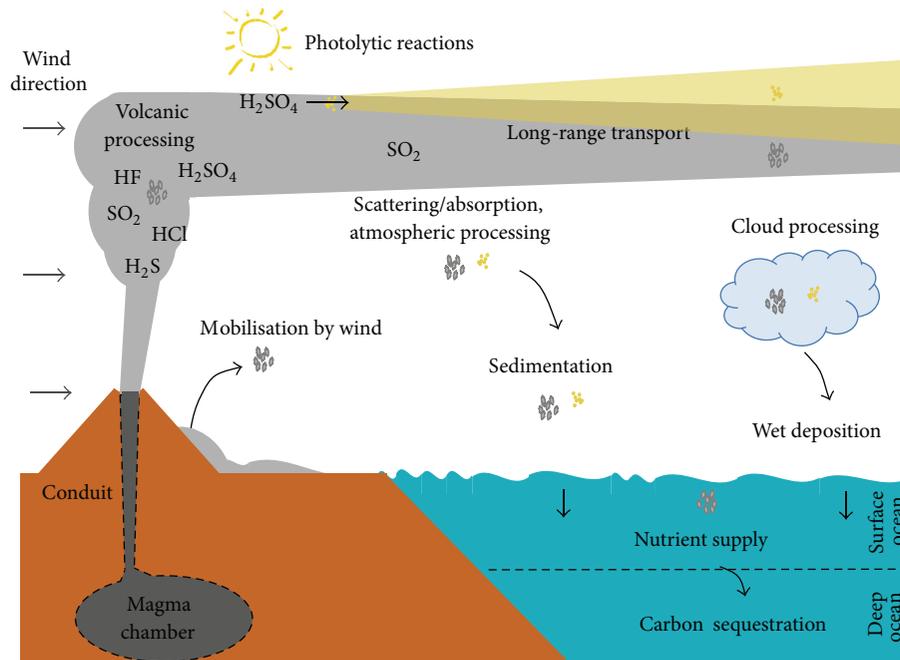


FIGURE 1: Schematic diagram showing the important processes controlling climate effects of volcanic ash (in grey) and volcanic sulphate (in yellow).

silicic magma chambers may be recharged with volatiles supplied by mafic magmas that have been differentiated in a lower crustal “hot zone”. At high pressure, supercritical fluids, which are formed by fractional crystallisation of vapour-saturated melts, trigger the exsolution of a few wt-% H_2O , CO_2 , and other volatiles and coexist with mafic melts or segregates from these compounds, that move independently through the crust [63]. Reference [64] presents evidence for deep degassing beneath Popocatepetl, Mexico, by showing melt inclusions with high concentrations of CO_2 and S (above 1000 and 2000 ppm, resp.) indicating that degassing begins at depths of at least 25 km. Two other mechanisms are proposed by [59] to explain the excess sulphur phenomenon: (a) eruption of bubble enriched magma and (b) degassing of a convective magma column. Another process leading to SO_2 formation taking place in the hot core of volcanic plumes is presented in [65] and is discussed in Section 2.3.

Reference [7] reports about the high-temperature scavenging of volcanic SO_2 by volcanic ash with potential important modifications of volcanic ash surfaces under cooler conditions. The authors suggest that extensive in-conduit SO_2 scavenging by tephra from 7 to 45% may take place during large eruptions where fragmentation of magma already occurs close to the magma chamber [66, 67]. Surprisingly, the interaction of SO_2 with tephra at high temperature in volcanic conduits and eruption plumes has long not been considered in discussions related to SO_2 scavenging [68–70]. Reference [7], however, points to a consumption process of volatile sulphur, which would increase the discrepancies between petrological and remote sensing measurements even more.

2.3. Chemical and Mechanical Processing in Volcanic Plumes.

The volcanic eruption plume is defined as the volume above the vent up to the level of neutral buoyancy (Figure 1) characterised by the major updraft motion. Turbulent motion dilutes the gas-particle mixture released from the vent by entraining ambient atmospheric water vapour into the plume thereby generating buoyancy. In addition, changes of the aggregation state of water redistribute energy in the volcanic eruption plume. In this volume volcanic ash and gases are cooled from about 1000°C to less than 0°C in only a few minutes [1, 31] and major fragmentation processes of volcanic ashes occur. The size distribution of volcanic ash is considerably dependent on the eruption conditions. During the eruption of a single volcano, the eruption conditions may change on timescales of seconds, so that fragmentation processes due to explosive eruptions (see Section 2.2), phreatomagmatic eruptions, pyroclastic flows, and coignimbrite clouds are superimposed. During phreatomagmatic eruptions [1], external cold water from, for example, glaciers (early phase of the Eyjafjallajökull eruption [71]), crater lakes, or the shallow ocean [72] chills the erupting hot magma. The subsequent shattering process leads to a powerful explosive eruption and an efficient production of fine-grained volcanic ash. Pyroclastic flows are resulting from collapsing eruption columns with low buoyancy producing impetuous tephra flows along the slopes of a volcano [1]. When the conditions at the top of a pyroclastic flow evolve to exceed the buoyancy of the ambient air, coignimbrite clouds can develop.

During basaltic eruptions, volcanic ash particles with diameters less than $30\ \mu\text{m}$ (PM_{30} , particulate matter with diameters smaller than $30\ \mu\text{m}$) represent a minor fraction

in contrast to rhyolitic eruptions, where a contribution of 30–50% to the total ash content is observed [3]. However, the knowledge about PM₁₀ and PM_{2.5} ash particles, which undergo long-range transport, is relatively sparse in the volcanology research community, although such small-scale ash particles have been observed in the atmosphere for several months after volcanic eruptions [33, 34]. Volcanic ash particle density varies between 2 and 3 g/cm³ [2, 73] and is a function of magma composition and fraction of crystallisation and porosity [74]. In addition, in the volcanic eruption plume, quenching processes may produce part of the glass material contained in volcanic ash. Beside the rapid cooling during updraft and entrainment of ambient air, lightning strokes in the volcanic eruption plume [75, 76] may contribute to quenching as well as to dry volcanic ash aggregation of charged ash particles (see Section 3) and to modifications of the volcanic ash and gas chemical composition, for example, incomplete crystallisation reactions (see Section 2.2).

According to [65], SO₂ injection into the atmosphere is not essentially generated directly from shallow or deep magma systems but it can be produced in the hot core ($T > 600^{\circ}\text{C}$) of a volcanic plume as the result of H₂S oxidation. The hot core of volcanic plumes is considered the main cause of changes in the sulphur speciation [77, 78]. Also, [79] showed that the redox state of magma recorded at depth does not necessarily mirror that of its escaping gases. Depending on the initial oxidation state, the hot core of a volcanic plume can function as a reactor for SO₂ formation and convert an initially SO₂-poor mixture (reflecting the petrologic estimate) to a SO₂-rich mixture (reflecting the remote sensing observation). Therefore, these studies represent another explanation for the differences in atmospheric measurements of SO₂ after volcanic eruptions and the source conditions (see Section 2.2).

Further chemical conversions of sulphur containing gases and particles take place in the mid- and low-temperature regions of volcanic plumes [8]. Reference [80] proposed a sulphuric acid dew point in the eruption plume of 338°C. However, this dew point temperature is only valid for very high concentrations of sulphuric acid at ambient pressure [81] and therefore only partly is a reasonable estimate for volcanic plumes. Reference [8] showed that $T \sim 150^{\circ}\text{C}$ and $\sim 50^{\circ}\text{C}$ are more reliable estimates for the dew point temperatures in volcanic plumes of sulphuric acid and water, respectively. After sulphuric acid condensation starts at $T \sim 150^{\circ}\text{C}$, the concentration of sulphuric acid droplets increases and reaches a plateau close to 50°C. At this temperature, water vapour condensation starts followed by the dissolution of the surrounding gases in the liquid water film [69]. Due to dissociation in liquid water, gaseous H₂SO₄ is rapidly depleted. Further physicochemical processes at temperatures less than 50°C, where due to the presence of a liquid water film around volcanic ash particles, aqueous chemistry reactions become increasingly important, are discussed in Section 2.4.

Also at temperature above 50°C (in the absence of liquid water), the gases and secondary compounds produced from the initial volcanic gases may react with volcanic ash within the eruption plume, thereby producing soluble compounds on the volcanic ash surfaces [68, 80, 82]. It is assumed that

30–40% of the sulphur species and 10–20% of the chlorine species, which are released during a volcanic eruption, are scavenged by volcanic ash [68, 83]. The presence of soluble compounds on volcanic ash surfaces has been shown by a number of leaching experiments with pristine volcanic ash in water [84]. Beside various sulphate and halide compounds, biologically relevant elements such as N, P, Si, Fe, Cd, Co, Cu, Mn, Mo, Pb, and Zn have been measured [35, 85, 86]. Different explanations for this leaching behaviour have been proposed in the literature [48], for example, adsorption of volcanic salts on volcanic ash surfaces [87, 88], condensation of sulphuric acid on volcanic ash surfaces [68], acid dissolution of ash surface material, and deposition of secondary minerals and salts on volcanic ash surfaces [89]. Altogether, the processes at the ash particle surfaces are incompletely understood until today [90], so improvements in the scientific understanding are urgently required.

2.4. Chemical Processing in Volcanic Clouds. Once the volcanic plume has reached neutral buoyancy conditions, the volcanic cloud spreads out quasi horizontally (Figure 1) and further chemical and microphysical modifications of sulphur containing compounds and volcanic ash surfaces take place at ambient temperatures. When volcanic ash and volcanic gases are released at different injection heights (e.g., 1991 eruption of Pinatubo; [91]), such interactions are limited. However, chemical reactions like acid processing on volcanic ash surfaces may occur when the major injection altitudes of volcanic ash and gas are similar (e.g., during the eruption of Kasatochi in 2008; [92]). Fast sedimentation of large volcanic ash particles also restricts the possibilities of volcanic ash and volcanic gases to interact. However, sedimentation of submicron volcanic ash particles is relatively slow, so they have been observed for months in the lower stratosphere, for example, after the 1991 Pinatubo eruption [33, 34], allowing the condensation of volcanic gases followed by acid processing of volcanic ash surfaces.

In the presence of volcanic ash, water vapour condensation on the volcanic ash surface starts at about 50°C. Gaseous sulphuric acid rapidly dissolves in this film of water and dissociates to H⁺ and HSO₄⁻, so more than 80% of the mass of the sulphuric acid is transferred out of the gas phase [8]. The scavenging of SO₂ by water depends on the availability of other acidic gases. In general, the solubility of acid gases decreases with increasing acidity of the aqueous phase. HCl has four orders of magnitude higher solubility than SO₂ and therefore hinders the scavenging of SO₂ [93]. Model simulations in the absence of HCl remove 15% of the SO₂ from the gas phase, whereas in the presence of HCl less than 5% of the SO₂ is scavenged by the liquid water and more than 99% of the HCl is removed out of the gas phase [8]. In contrast, H₂S is only slightly soluble in liquid water, so its removal by cloud and raindrops at lower altitudes is negligible [31].

In the troposphere, cloud processing drives the efficient uptake of acid gases by aerosols [94], including volcanic ash particles [95]. As the lifetime of clouds is limited, they

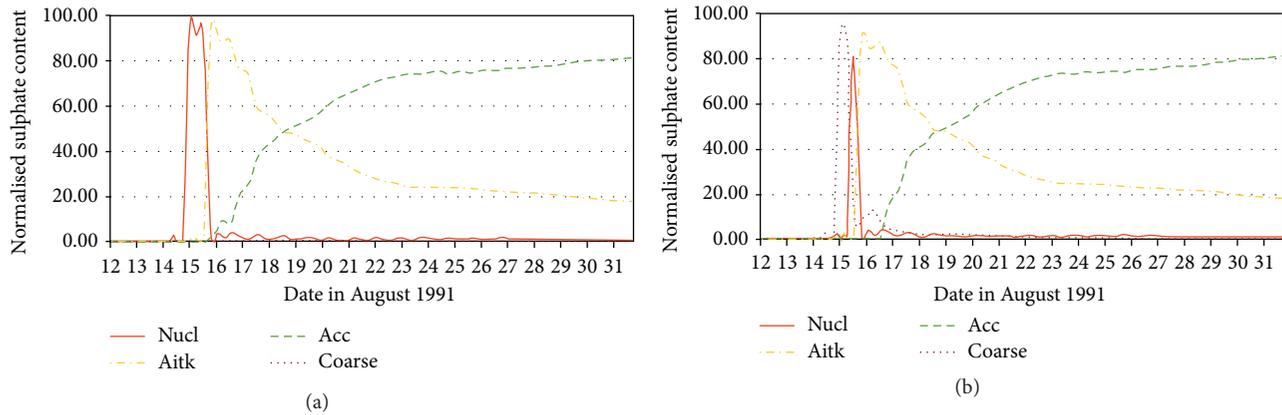


FIGURE 2: Modelled size distribution of sulphate aerosols during and after the 1991 volcanic eruption of Mt. Hudson (a) without and (b) with volcanic ash, normalised to the total amount of sulphate (100%). Red line: nucleation mode; yellow line: Aitken mode; green line: accumulation mode; brown line: coarse mode.

can form and evaporate several times [94] during the long-range transport of volcanic ash particles in the atmosphere. After evaporation of cloud water, the thin film of aqueous electrolyte around each particle may reach pH values smaller than 2 [96, 97]. Such low pH values contribute considerably to, for example, iron solubility in aerosols like mineral dust [98–100], but until today, the scientific understanding of these processes remains limited. Only a few studies investigated atmospheric processing of volcanic ash and gases at freezing temperatures, indicating considerable scavenging of volcanic gases like SO_2 , H_2S , and HCl by ice particles and increased iron solubility [69, 101].

During ash-free volcanic eruptions or when volcanic gases and their secondary products are separated from volcanic ash and SO_2 and H_2S are injected into the stratosphere, they are mainly oxidised by reactions with OH to sulphuric acid on a timescale of days to weeks [6, 94, 102]. Sulphuric acid vapour is further converted to sulphate aerosols through the formation of new particles via binary homogenous nucleation involving sulphuric acid vapour and water vapour. This was observed after the 1991 eruption of Mt. Pinatubo, with an increase of 1–2 orders of magnitude in the concentration of condensation nuclei [103] and by 98% of the observed stratospheric aerosol being volatile [104, 105]. The condensation of sulphuric acid vapour onto existing particles shifts the particle size distribution to greater radii [106]. Coagulation of aerosols represents another particle growth process, which is a function of particle size and particle number concentration [107]. Observations after the 1991 Pinatubo eruption indicate that it takes about three months to reach a peak in stratospheric sulphate aerosol concentrations [34, 103]. The sulphate aerosol particle density is assumed to lie in the range from 1.6 to 2.0 g/cm^3 [49, 108–110].

An exemplary model simulation study during the 1991 Mt. Hudson volcanic eruption in Chile illuminates the sulphate aerosol development [111]. In the absence of volcanic ash (Figure 2(a)), the sulphate aerosol formation process starts through nucleation ($d < 0.01 \mu\text{m}$) on August 14. By August

16, condensation and coagulation drive the formation of Aitken mode sulphate particles ($d: 0.01\text{--}0.1 \mu\text{m}$, named after John Aitken), which further grow into the accumulation size mode ($d: 0.1\text{--}1.0 \mu\text{m}$), which forms the dominating mode from August 19 onwards. In the presence of volcanic ash (Figure 2(b)), coarse mode sulphate aerosols ($d > 1 \mu\text{m}$), which are formed by condensation of sulphuric acid vapour on coarse mode volcanic ash, dominate during the first hours of the eruption. Due to rapid sedimentation of volcanic ash, these coarse particles are soon separated from the gaseous sulphur containing atmospheric layers, so sulphate aerosol formation occurs mainly through nucleation later the day. The further development in sulphate aerosol size distribution is comparable to the non-volcanic ash situation. When submicron volcanic ash particles are injected into the stratosphere, they may survive in the lower stratosphere for months due to their slow sedimentation [33, 34]. In the presence of SO_2 and its oxidation products, volcanic ash is coated with aqueous H_2SO_4 with potential subsequent effects on the solubility of minerals at the volcanic ash surface (see Section 4.4).

3. Atmospheric Burden, Residence Time, and Deposition

Volcanic ash and sulphate atmospheric concentrations are highly variable in space and time dependent on the volcanic activity, the location of a volcanic eruption, and the atmospheric dispersion patterns upwind from the volcano. Volcanic ash mass concentrations measured in the troposphere during the eruption of Eyjafjallajökull, Iceland, in 2010, range from daily mean near surface concentrations of 400 $\mu\text{g}/\text{m}^3$ in Scandinavia [112] to maximum ash concentrations of about 4000 $\mu\text{g}/\text{m}^3$ in the volcanic ash cloud transported over Europe [112, 113]. On Iceland, daily average near surface concentration exceeded 1000 $\mu\text{g}/\text{m}^3$ during the ongoing eruption of Eyjafjallajökul and also afterwards during resuspension events [15]. For a more detailed summary

on volcanic ash resuspension events after various volcanic eruptions (Eyjafjallajökull 2010; Hudson 1991; Katmai, 1912) see [48].

In the lower stratosphere, [114] discovered a sulphate aerosol layer under undisturbed conditions with a global sulphate load in the order of 0.15 Tg Sulphur [115]. Volcanic sulphate aerosols significantly enhance this stratospheric background sulphate concentration over a couple of years [6]. The e-folding decay time of stratospheric sulphate is approximately one year [116–119]. Once injected or formed in the stratosphere, SO₂ and sulphate particles are rapidly advected around the globe. After the 1883 Krakatau eruption, sulphate aerosols circled the globe within two weeks [120]. The volcanic sulphate aerosols from the 1982 El Chichón [121] and 1991 Pinatubo cloud [122] required three weeks to circle the globe. Volcanic gases and particles produced from high-latitude volcanic eruptions may encircle the poles faster due to the shorter pathway and higher wind speed. Mt. Hudson, Chile (1991) emissions were transported around Antarctica in 10 days [123, 124]. About two weeks were necessary for volcanic emissions from Kasatochi, Alaska (2008) (http://www.doas-bremen.de/images/highlights/gome2_so2_kasatochi_large.gif), and Puyehue-Cordón Caulle, Chile (2011), to travel around the pole. For tropical volcanic eruptions, the normal residual stratospheric meridional circulation lifts the sulphate aerosols in the tropics [6], from where they are transported poleward and returned back into the troposphere at higher latitudes on a timescale of 1–2 years [125–127].

The injection height [94] into the atmosphere is a major controlling factor for the residence time of aerosols. Generally, higher injection heights result in higher residence times [128]. However, the amount of aerosols and volcanic ash represents another controlling factor. High stratospheric concentrations of sulphate aerosols do not necessarily persist longer in the stratosphere than moderate concentrations. The higher the stratospheric concentrations of sulphate aerosol particles, the higher the collision rates, which cause larger particle sizes and faster fallout and consequently shorter lifetime of the volcanic aerosols [129]. In the presence of volcanic ash, when sulphate condensation on ash surfaces takes place (see Section 2.4), the atmospheric lifetime of sulphate aerosols is also reduced due to the faster sedimentation of the relatively large ash particles.

During sedimentation in the atmosphere, sulphate aerosols are at or very close to their terminal fall velocities, which are given by the Stokes–Cunningham formula [130]. In the troposphere, washout and rainout represent the major removal processes of sulphate aerosols [131]. Gravitational settling of volcanic ash has often been observed to exceed the terminal fall velocity of single ash particles [132, 133]. Volcanic ash aggregates consisting of numerous ash particles attached to each other in an ice-ash-mixture or by electrostatic forces explain this behaviour [134–136], which leads to increased sedimentation close to the volcano and reduced atmospheric volcanic ash concentration during long-range transport. However, the scientific knowledge on major aggregation formation processes is still limited [48, 133].

Deposition of sulphate and volcanic ash onto ice covered surfaces, into the ocean, on peat, and so forth can be reconstructed from historical archives (namely ice, peat, sea, and ocean sediment), which may provide useful information on past volcanic activity [137, 138]. High-quality ice core records on acidity as surrogate for volcanic sulphate deposition are restricted to the last 1000–1500 years [32], with decreasing quality as depth is increased. Based on marine sediment core data, reference [37] estimated the millennial scale flux of volcanic ash into the Pacific Ocean to about 128–221 Tg/yr.

4. Climate Forcing

4.1. Direct Radiative Effects: Absorption/Scattering of Sunlight/Long-Wave Radiation. When volcanic ash is released into the atmosphere during volcanic eruptions or remobilisation events, it reduces visibility and solar irradiation reaching the earth's surface thereby cooling the earth's surface [139]. The short atmospheric residence time of the majority of volcanic ash restricts its direct radiative effects (and indirect radiative effects, see Section 4.2) to the region close to the eruption and along the major transport pathways in the atmosphere, where, however, the direct radiative effects of volcanic ash may be dominant [48].

However, the major global direct radiative effects after volcanic eruption result from stratospheric sulphate aerosols [6, 31]. They scatter incoming shortwave solar radiation, thereby, leading to a cooling of the earth's surface and counteracting global warming. Therefore, the injection of sulphate aerosols into the stratosphere is a proposed geoengineering technique [110, 140] to counteract global warming, which is however discussed very controversially with respect to technical solutions, costs, efficiency, side effects, and ethical issues [141]. In addition to sulphate aerosols, volcanic ash particles have been observed for several months in the lower stratosphere following major volcanic eruptions [33, 34]. They may become coated with aqueous H₂SO₄ and can also contribute to the cooling of the earth's surface. Sulphate aerosols also absorb and emit radiation in the near-infrared spectral range thereby heating the stratosphere [6].

4.2. Indirect Radiative Effects: Cloud Condensation and Ice Nuclei. In the troposphere, volcanic sulphate aerosols and ash can act as cloud condensation nuclei (CCN) and ice nuclei (IN). The increase in cloud droplet number concentrations in the presence of aerosols, which modifies the cloud radiative properties, is referred to as the first indirect effect [142]. The second indirect effect [143] describes the aerosol effect on lifetime and precipitation formation of clouds. Volcanic sulphate aerosol in the troposphere is either formed from volcanic SO₂ emissions released into the troposphere or results from downward transport from the stratosphere by sedimentation. In comparison to the direct radiative impact of volcanic sulphate aerosols in the stratosphere, the indirect effect is of minor importance, although it may have considerable local effects, such as the modification of precipitation. An initial suppression of precipitation leads to an increase of liquid water and water vapour staying in the atmosphere, which may

trigger heavy precipitation events [144]. Therefore, aerosols including volcanic ash and sulphate, which act as CCN [145, 146] and IN (see below), have the potential to affect the earth's radiation budget and the hydrological cycle locally, regionally, or in some cases, globally [147]. In supercooled clouds, the presence of particulate material, such as volcanic ash [95, 148–150], may initiate heterogeneous nucleation of ice crystals at significantly lower supersaturations and higher freezing temperatures than in the case of homogeneous freezing [148]. Atmospheric and volcanic processing including modifications of the surface chemical composition of volcanic ash particles (see Section 2) have implications for their behaviour to act as CCN or IN and to release nutrients (in particular iron) in contact with seawater (see Section 4.4).

4.3. Other Radiation Induced Indirect Climate Effects. The radiative effects of stratospheric sulphate aerosols released in particular from tropical volcanic eruptions (see Section 4.1) trigger several modifications of the global climate system [6], which remain to be fully understood until today. Stratospheric warming caused by volcanic sulphate aerosols decreases the tropopause height [151]. In addition, the pole-to-equator temperature gradient in the lower stratosphere is increased [6]. As the circulation in the stratosphere and troposphere is coupled, the polar vortex is strengthened amplifying circulation patterns and creating increased surface temperature during winter in the northern hemisphere. For a detailed description, the reader is referred to [6]. Stratospheric ozone concentrations are reduced by heterogeneous reactions on volcanic sulphate aerosol surfaces. Modifications in sea level height [152], river run-off [153], and tropical precipitation [154] are reported. Additional nonlinear climate feedbacks, for example, between the atmosphere and the ocean heat content and dynamics [155] or the terrestrial vegetation [156] are assumed to modify atmospheric CO₂. However, due to the complexity of the climate system, it still remains open if modifications in the global carbon cycle after volcanic eruptions can fully be explained with radiation induced effects after volcanic eruptions. As the last three major tropical volcanic eruptions (Agung, 1963; El Chichón, 1982; Pinatubo, 1991) coincided with substantial El Niño events, it has been proven difficult to separate climate response due to El Niño, volcanic forcing, or the combined effect [157].

4.4. Iron Fertilisation of the Surface Ocean. Many biological functions in marine plankton depend on trace metals that are scarce in the ocean but that are contained in volcanic ash. Especially, iron is required for many important oceanic biogeochemical processes such as cellular processes, photosynthesis, respiration, nitrogen fixation, and nitrate reduction. In High-Nutrient-Low-Chlorophyll (HNLC) ocean waters [158] (Southern Ocean and northern and equatorial Pacific), iron represents the major limiting component for marine primary production (MPP). This “iron hypothesis” was introduced by [159]. Iron supply to these ocean waters affects MPP and phytoplankton growth, which in turn influences the development of higher trophic levels of the marine food chain. The

biological CO₂ pump of the ocean is stimulated due to the build-up of organic carbon in the surface ocean and descend to the deeper ocean. Thereby atmospheric CO₂ is reduced. Finally, a reduction of atmospheric CO₂ concentrations is triggered as the surface ocean CO₂ concentration reequilibrates with the atmospheric CO₂ concentration. Today, the effects of ocean iron fertilisation on the global carbon cycle are discussed controversially, specifically, in the context of climate engineering.

During the past few years, several studies highlighted the influence of volcanic ash on the biogeochemistry of the surface ocean [35–39] via the dissolution of trace species, in particular iron compounds, in water [85, 160]. Beside iron compounds, volcanic ash can release additional trace metal salts containing, for example, copper and zinc, which are known for their fertilising as well as toxic effects on plankton [38].

According to [37], volcanic ash deposition fluxes to the Pacific Ocean are comparable to the mineral dust flux into the Pacific Ocean of ~100 Tg/yr [161]. Yearly mineral dust deposition into the ocean may, however, be well below the deposition of volcanic ash during major volcanic eruptions. During and after the eruption of Mt. Hudson in Chile (August 12–15, 1991), the ocean iron deposition connected to volcanic ash corresponds to about 500 years of iron deposition connected to mineral dust from Patagonia [162]. For a detailed comparison of volcanic ash versus mineral dust environmental and climate effects see [48].

Another effect on climate induced by ocean iron fertilisation is associated with a potentially increased flux of organic carbon (OC) containing sea-spray aerosols [163] and dimethyl sulphide (DMS) [164], which may be oxidised to sulphate aerosols. Sulphate and OC aerosols may form CCN's contributing to the indirect aerosol effects ([165]; see Section 4.2).

4.5. Climate Effects of Volcanic Sulphate versus Volcanic Ash

4.5.1. Effect on Atmospheric CO₂. Due to backscattering of solar radiation to space, volcanic sulphate aerosols can counteract the global temperature increase, which is driven by the increasing atmospheric load of greenhouse gases. Therefore, artificially injected sulphate aerosols into the stratosphere have been proposed as one possibility of climate engineering, also called geoengineering (“the deliberate change of the earth's climate by mankind”). Although, theoretical studies show that it is possible to cool the earth [110], it is unlikely that the climate system will return to the state prior to human-induced CO₂ increase. In addition, unwished side effects cannot be excluded. It is also clear that this geoengineering method will not reduce CO₂ uptake by the ocean and ocean acidification [166], as atmospheric CO₂ concentrations are not directly affected. However, indirect effects on the atmospheric carbon cycle, for example, more CO₂ uptake by vegetation [156] due to increased diffuse radiation [167], are discussed in the literature.

Another technique of geoengineering is ocean fertilisation by iron. Although several issues concerning the

efficiency of the biological carbon pump of the ocean are in discussion [158], this method is supposed to counteract global warming by reducing atmospheric CO₂ thereby preventing ocean acidification. Beside mineral dust, volcanic ash represents a natural iron fertiliser of the ocean. Reference [158] explains only 25% of the observed CO₂ decrease during glacial maxima with ocean iron fertilisation by mineral dust. Ocean fertilisation by volcanic ash and the subsequently enhanced efficiency of the biological carbon pump provide an additional explanation for the decrease in atmospheric CO₂ during the geological past [168]. The following subsections contrast climate forcing by ocean iron-fertilisation with volcanic ash with climate forcing by radiation-induced effects of volcanic sulphate.

4.5.2. Specific Eruptions

(a) *Kasatochi, Alaska, August 2008, VEI 4 (52.2°N, 175.5°W)*. The volcano Kasatochi on the Aleutian Islands erupted in August 2008. Shortly after this eruption an unusual phytoplankton growth was observed in the NE Pacific [36, 42–44]. Seawater CO₂ partial pressure at the ocean station Papa decreased by about 40 ppm. This textbook example of the development of a massive and large-scale phytoplankton bloom represents the first direct proof of the potential of volcanic ash to fertilise the surface ocean. Two years later, a discussion on the linkage between increased sockeye salmon population in the Fraser River in Canada and ocean iron fertilisation by volcanic ash from Kasatochi started [169–171].

The total volcanic ash flux released from Kasatochi is estimated by 0.2–0.3 km³ DRE (Dense Rock Equivalent) [92]. In comparison with major volcanic eruptions (see below) Kasatochi ash emissions are relatively low. According to [42], the stimulation of the biological CO₂ pump by the iron fertilisation with volcanic ash from Kasatochi results in a reduction of atmospheric CO₂ by about 0.01 Pg C. This amount of carbon sequestration represents a negligible fraction compared to rise of CO₂ emissions resulting from fossil fuel combustion (7–9 Pg C/yr; [172]).

The Kasatochi eruption injected 1.4–2.0 Tg SO₂ [92, 173, 174] into the lower stratosphere. The development of a stable stratospheric sulphate aerosol layer between 15 and 21 km at mid to high northern latitudes took place within 4–6 weeks after the eruption [173]. Maximum AOD (Aerosol Optical Depth) at 750 nm was approximately a factor of two above the background value and eventually returned to background levels by March 2009. Although the SO₂ injection into the stratosphere by the Kasatochi eruption represents the largest volcanic injection of SO₂ into the stratosphere since 1991 and the strength of the eruption is characterised by VEI = 4, the eruption of Kasatochi in August 2008 caused negligible climate effects due to stratospheric sulphate [175] and ocean fertilisation [42].

(b) *Mt. Hudson, Chile, August 1991, VEI 4 (45.9°S, 72.9°W)*. The volcanic eruption of Mt. Hudson took place in August 1991, only two months after the eruption of Pinatubo in June

1991 (see below). Therefore, climate effects associated with the Mt. Hudson eruption are nearly always assessed together with those of the stronger Pinatubo eruption, but often as a minor side effect. Approximately 1.1 km³ of ash was directly supplied to the iron-limited Atlantic sector of the Southern Ocean [176]. Ash fallout was also recorded on the Falkland Islands (~1.000 km SE from the volcano; [177]) and South Georgia (~2.700 km SE from the volcano; [178]). This ash deposition into the ocean—although it considerably exceeds the possible amount of ash from Pinatubo that was potentially deposited in the Southern Ocean—has never before been taken into account as an explanation for the decrease in atmospheric CO₂ concentration of 1–2 ppm after 1991 [40]. The global climate in 1991 was also influenced by an El Niño event [157]. The usual increase in atmospheric CO₂ concentrations during El Niño events, however, did not take place in 1991 [179]. The reasons are hidden in the until today not fully understood nonlinear climate feedbacks after major volcanic eruptions (see Section 4.3). Most probably, the direct fertilisation effect of the ocean by iron with Mt. Hudson ash was partly inhibited by the absence of sunlight during southern hemispheric winter. However, after the Mt. Hudson eruption about 1.6 km³ DRE was deposited in Patagonia. The dry and windy conditions in this region cause efficient remobilisation of the ash into the atmosphere [12]. When transported towards the ocean, this ash is eventually available for ocean fertilisation. As satellite ocean colour data are only randomly available before 1997 (<http://oceancolor.gsfc.nasa.gov>), coupled biogeochemical ocean-atmosphere modelling or the analysis of the young parts of historical archives like peat cores or lake sediments located downstream of Mt. Hudson may shed some light on such a hypothesis. The Falkland Islands located about 1500 km southeast from Patagonia in the downstream direction offer ideal conditions for peat accumulation and analysis of volcanic ash in peat [180, 181].

During the Mt. Hudson eruption, the injected amount of SO₂ into the stratosphere was similar to the Kasatochi eruption (1.65 Tg SO₂; [124]). The southern hemispheric AOD in higher latitudes from August 23 until September 30 clearly indicates the stratospheric sulphate originated from Mt. Hudson (Figure 3). Through Lidar and satellite measurements over Antarctica, the Mt. Hudson sulphate cloud was observed between 9 and 13 km within the polar vortex from August to October 1991 [182, 183]. However, the Mt. Hudson stratospheric sulphate load and the subsequent global climate forcing by reduced solar irradiation can only be partly separated from the higher stratospheric sulphate loading produced from the Pinatubo eruption (Figure 3). Therefore, for climate effects induced from the stratospheric sulphate load, see the discussion below associated with the Pinatubo eruption.

(c) *Mt. Pinatubo, Philippines, June 1991, VEI 6 (15.1°N, 120.3°E)*. The Pinatubo eruption represents one of the largest SO₂ injections into the stratosphere since the beginning of the 20th century with approximately 20 Tg SO₂ [122]. After the eruption, a global average cooling of 0.4 K occurred at the earth surface [172, 184, 185] and an increase in

SAGE II 1020 nm optical depth

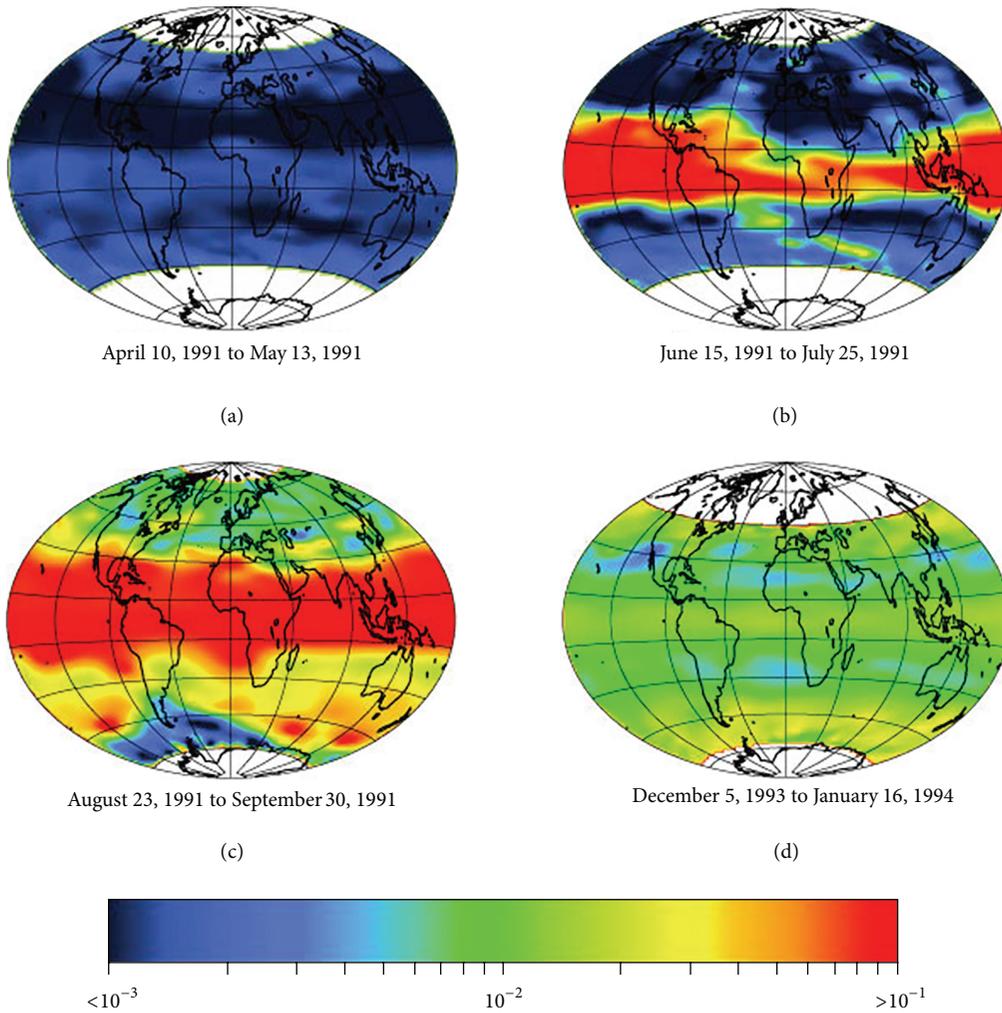


FIGURE 3: Aerosol optical depth. Eruption of Pinatubo: June 15, 1991; eruption of Mt. Hudson: August 15, 1991 (Courtesy of NASA).

stratospheric temperatures of 2-3 K was observed [186]. The direct radiation at the Mauna Loa observatory on Hawaii was reduced by $\sim 140 \text{ W/m}^2$, whereas diffuse radiation increased by $\sim 100 \text{ W/m}^2$ [6]. Also, reduced atmospheric CO_2 concentrations of around 1-2 ppm were observed [40]. Reference [156] argued that this was a consequence of increased vegetation photosynthesis due to diffuse radiation induced by the presence of the volcanic sulphate aerosol layer in the atmosphere. References [40, 41] suggested that the atmospheric CO_2 drawdown was the result of ocean fertilisation by Pinatubo ash, which reached the Southern Ocean by November 1991. However, the majority of the volcanic ash released during the 1991 Pinatubo eruption ($5\text{-}6 \text{ km}^3$ DRE; [91]) was deposited in or nearby the South China Sea [187]. Only a few percent reached the iron-limited Southern Ocean. Therefore, it is more likely that a climate effect by ocean fertilising within the Southern Ocean is negligible. However, as outlined above, Southern Ocean fertilisation by volcanic ash from the Mt. Hudson eruption

needs further investigations. By taking into account the radiative effect of stratospheric sulphate from volcanic origin only, indirect effects on the climate system cannot fully be explained, for example, by global climate model simulations [188] in particular after the 1991 Pinatubo eruption. However, it remains open, if yet unknown feedback mechanisms in the climate system or unconsidered processes, such as the ocean fertilisation by volcanic ash with iron, may offer satisfactory explanations.

(d) Mt. Katmai, Alaska, June 1912, VEI 6 (58.2°N , 154.9°W). The world's largest volcanic eruption of the 20th century took place at Novarupta, Alaska. Most of the magma vented at Novarupta was stored beneath Mt. Katmai, therefore, both names appear in the literature. During the eruption, about 13 km^3 DRE of volcanic ash [189] and 5 Tg SO_2 [190] were injected into the atmosphere. The volcanic ash cloud was transported to west-south-west directions with ash fall over the Gulf of Alaska and Northern America [191]. According to

[44], ocean fertilisation of the NE Pacific during the month of June has the potential to increase phytoplankton concentrations thereby stimulating the ocean biological pump, which reduces atmospheric CO₂ concentrations. Phytoplankton production in the NE Pacific is even more efficient from July until October [44] if iron is supplied to the ocean. According to [191], the loose volcanic ash deposits around Katmai produced ash clouds throughout the summer of 1912 through remobilisation by wind thereby providing further iron for the fertilization of the NE Pacific Ocean. But, as time goes by, repeated rainfall in the depositional area may diminish the iron contained in the surface rim of volcanic ash through leaching. Many kilometres long pumice rafts released from the Katmai eruption have been observed in the coastal waters of the Gulf of Alaska even decades after the Katmai eruption [188], which can supply iron for the fertilisation of the ocean as well [192]. However, as the area of the NE Pacific that may have been fertilised with iron from the volcanic ash and pumice released from Mt. Katmai is much smaller than that after the Kasatochi eruption in 2008 [36, 92, 191], a climate effect induced by ocean fertilisation is probably negligible. In addition, the radiative effect due to volcanic sulphate from Mt. Katmai was restricted to the Northern Hemisphere [190] and has therefore limited global climate effects as well.

(e) *Huaynaputina, Peru, February 1600, VEI 6 (16.6°S, 70.8°W)*. The eruption of Huaynaputina volcano in Peru in February 1600 AD was the largest historically recorded eruption in South America with a VEI of 6 and globally one of the largest events during the past 2000 years. The eruption produced more than 9.6 km³ DRE of volcanic ash [193]. Ash fallout was reported throughout southern Peru, northern Chile, and western Bolivia and is also known to have settled into the tropical Pacific as well as the Southern Ocean, two large HNLC areas. Volcanic ash particles from the Huaynaputina eruption have been identified in Antarctic ice cores [194], thereby, confirming the large-scale transport of volcanic ash from the Huaynaputina eruption to the Southern Ocean. Numerical model studies of volcanic ash dispersion and deposition after the eruption of Huaynaputina in 1600 will be necessary during typical climate conditions such as El Niño and La Niña and normal years to reconstruct the major depositional areas and fluxes into the ocean. This should be followed by ocean biogeochemical modelling in order to determine the ocean biogeochemical response on fertilisation by Huaynaputina volcanic ash. An iron-fertilisation effect may partly explain the 10 ppm decrease in atmospheric CO₂ concentration measured in Antarctic ice cores after 1600 [195]. However, as no δ¹³CO₂ measurements are available, [195] conclude that it is unclear whether the initial CO₂ decrease at AD 1600 was driven by changes in the carbon exchange rates between the atmosphere and the ocean or the terrestrial biosphere.

Reference [196] reports that the most severe cooling of -0.81 K in the Northern Hemisphere during the past 600 years occurred in 1601. The authors speculate if in addition to the Huaynaputina eruption a yet unidentified eruption

occurred at the same time or if the climate effect of the Huaynaputina eruption has been greatly underestimated. This is because the cooling is greater than is suggested by the degree of acidity in the various ice core records from which the stratospheric sulphate load is determined. Reference [193] estimates a global stratospheric loading of ~70 Tg H₂SO₄ due to the Huaynaputina eruption based on ice core data, whereas [197] reports ~80–170 Tg H₂SO₄ based on petrological analysis. These estimates greatly exceed the stratospheric H₂SO₄ load after the 1991 Pinatubo eruption (~30 Tg H₂SO₄; [16]). Due to the high uncertainties connected with the stratospheric sulphate loading and with indirect effects of reduced solar irradiation (see Section 4.3), a climate effect induced by volcanic ash ocean fertilisation can neither be confirmed nor excluded. Climate modelling studies including the volcanic ash ocean fertilisation effect may shed more light on the relevant processes affecting climate after major volcanic eruptions.

4.5.3. *Geological Records*. Many reasons for millennial climate change have been discussed in the literature, for example, tectonic motion, orbital variations, modifications in cosmic ray fluxes, silicate weathering in orogens, and volcanism [168]. Until recently, the discussion of volcanic forcing on climate on geologic timescales was restricted to radiative effects of stratospheric sulphate and further indirect effects (see Section 4.3; [198]). Although the occurrence of volcanic glass in deep-sea sediments has been regarded as indicator for volcanic activity, [199] did not consider ocean fertilisation by volcanic ash as a trigger for millennial climate change. However, it still remains unclear if even a megavolcanic eruption may trigger climate cooling on at least century timescale solely through radiative effects of stratospheric sulphate. The most recent major ignimbrite eruption was at Toba, Sumatra, about 75 ka ago. Toba erupted ~2500 km³ DRE [200]. Cooling related to the Toba eruption lasted about 1000 years [200]; however, recent studies suggest a weaker temperature response [201]. There is ongoing discussion about the stratospheric sulphate burden, its residence time, and climate forcing. Although much of the Toba ash was deposited in the Bay of Bengal [202], today an area in which marine primary productivity is not limited by the availability of iron, ocean iron fertilisation has not yet been considered to contribute to climate variability after the Toba eruption.

By analysing Antarctic ice cores on millennial time periods, [203] concluded that in addition to the volcanic sulphate effects on planetary albedo, volcanic ash may increase soluble iron in large surface areas of the nutrient limited Southern Ocean thereby stimulating growth of phytoplankton and affecting the global carbon cycle. These two effects together are supposed to trigger cooling during the last millennium [203]. Also [168, 204] present geochronologic and biogeochemical data suggesting that iron fertilisation by volcanic ash provides a plausible mechanism for atmospheric CO₂ drawdown during the Cenozoic climatic transition (about 33.5 Ma ago, near the Eocene-Oligocene boundary, when major continental glaciation in Antarctica began), both in terms of timing and biogeochemical mass balance.

Iron fertilisation by repeated ignimbrite eruptions may have accelerated the global cooling by the stepwise forcing of the climate across a climatic threshold, via the cumulative effect of CO₂ drawdown by hundreds of volcanic fertilisation events (note that the distribution of HNLC areas in ancient oceans was probably different from today, but remains poorly understood). This hypothesis suggests that repeated episodes of oceanic iron fertilisation by great volumes of rhyolitic ash might be sufficient to initiate cold climatic modes. Other studies also suggesting that the positive carbon isotopic anomaly near the Eocene-Oligocene boundary can be interpreted by record enhanced marine production and burial of organic carbon that led to decreased atmospheric CO₂ and global cooling are published by, for example, references [205–207]. This explanation is also proposed for the Cretaceous Ocean Anoxic Event 2 (about 94 million years ago; [208]) and for the younger Northern Hemispheric glaciation (about 2.75 million years ago; [209]). Reference [210] presented a close correlation between iron input and marine export production for the sub-Antarctic Atlantic based on a multi-proxy dataset from marine sediment cores for the last 1.1 million years. Their results imply that the process of iron fertilisation on marine biota was a recurring process operating in the sub-Antarctic region over the glacial/interglacial cycles. Mineral dust is made responsible for a CO₂ decrease of 25% during the last glacial maxima [158]. An overall assessment of the role of volcanic ash fertilisation of the ocean on atmospheric CO₂ on geological timescales in comparison to mineral dust effects will be necessary to increase our understanding of the processes contributing to natural climate variability.

5. Outlook

After the recent major volcanic eruptions like El Chichón (1982) or Pinatubo (1991), ground-based and satellite based observations of the volcanic stratospheric sulphate burden and distribution as well as, for example, modifications in atmospheric CO₂, solar radiation, and atmospheric temperature are available. These clearly reveal the importance of volcanic stratospheric sulphate in cooling the earth surface, which induces a number of further indirect effects on climate via nonlinear reaction and feedbacks in the climate system (see Section 4.3; [6]). Thereby, the earlier belief that volcanic ash particles suspended in the atmosphere are responsible for volcanic climate forcing [24] has been revised [2] and climate impacts induced by volcanic ash were no longer in the focus of research. Most of the interpretations of the climate effects after volcanic eruptions are based on climate model simulations driven by stratospheric volcanic sulphate forcing. However, until now, global climate models have difficulties to reproduce the observed variability of the earth system after large volcanic eruptions [188]. Either important feedback mechanisms have been overseen or still missing processes like ocean fertilisation by volcanic ash have not been taken into account. Therefore, it will be necessary to reinvestigate historical volcanic eruptions and their climate impact including the oceanic iron-fertilisation potential of volcanic ash. This is dependent on the geographical location

of an erupting volcano, the amount of volcanic ash deposited into the ocean directly after an eruption or post-eruptive through remobilisation of ash from deposits, the availability of macronutrient, and micronutrient in the adjacent ocean areas and the atmospheric conditions.

Generally, the largely overseen aspect of volcanic induced climate variability by ocean fertilisation urgently needs to be better assessed. This also holds for the role of volcanic ash fertilisation of the ocean in comparison with mineral dust ocean fertilisation [48] to better understand natural climate variability on geological timescales. Therefore, this review intends to trigger interdisciplinary investigations involving ocean biogeochemistry and biology, volcanology, geochemistry, meteorology, atmospheric chemistry, and climate research groups. To increase our current understanding of the volcanic ash fertilisation potential of the surface ocean, it will be necessary to achieve further knowledge about the iron processing in volcanic plumes and during long-range transport by conducting modelling studies and measurements in the field and laboratory. In addition, it is necessary to clarify how volcanic ash, as a so far neglected constituent in the marine environment, influences marine productivity and species composition, two main factors that affect marine carbon cycling and thus global climate.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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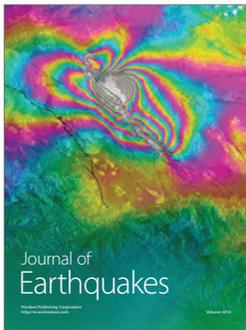
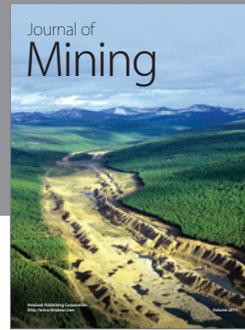
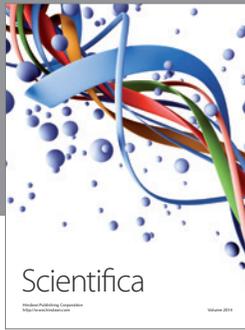
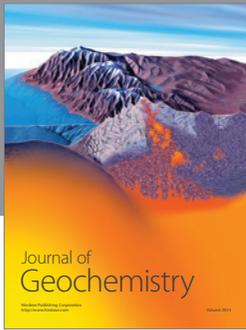
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