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Review

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Volcanic ash impacts on marine primary productivity: A review

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A growing body of evidence indicates that episodic volcanic ash deposition on the ocean surface is an important driver of marine biogeochemical change, as ash particles can supply a range of bioavailable micronutrients (including iron) to nutrient-poor oceans, influencing phytoplankton blooms. Understanding the variable nature and timing of ash impacts on marine primary productivity is essential, as phytoplankton play a central role in the marine food web, carbon cycling, and climate regulation. This review assesses existing research on volcanic ash deposition on the ocean and its effects on marine phytoplankton. We particularly focus on different research methods, their limitations, and knowledge gaps, including the impacts of large-scale eruptions in the geological record. To do this, we summarise datasets from direct observations, laboratory incubation experiments, and remote sensing, and explore novel proxy records from ice cores which may preserve evidence for past ash-phytoplankton interactions. Although several historic eruptions have been linked to short-term iron fertilisation effects on phytoplankton, the severity and duration of volcanic ash impacts on primary productivity remains poorly understood. In particular, the influence of variable ash chemical composition (namely fractional iron solubility), and deposition volume on phytoplankton bloom duration, species-specific responses, and longer-term ecological effects from large explosive eruptions, are still largely unknown. While current research demonstrates that ash input can stimulate primary productivity, the response is highly variable and depends on eruption magnitude, ash chemistry, the bioavailability of iron and trace metals, and oceanographic context. Chemical processing within the volcanic plume is also an important factor for enhancing the iron solubility within ash. Furthermore, we highlight that the indirect effects of eruptions, such as reduced light penetration to the surface ocean from ash clouds, and changes in atmospheric and thus sea surface temperature (SST), remain underexplored but may be significant in the context of larger events. We highlight the importance of bridging the gap between modern observations and the geological record using novel proxies, which is vital for understanding the extent to which voluminous, widespread volcanic ash deposition may impact global marine ecosystems.

Key words: volcanic ash, marine productivity, phytoplankton, trace metals, iron solubility

1. Introduction

Phytoplankton are microscopic, photosynthetic organisms found worldwide in aquatic environments, most abundant in the surface waters of nutrient-rich regions. Major phytoplankton groups differ in size and roles in biogeochemical cycling, and together are responsible for half of global primary production (Litchman et al., 2015; Anderson et al., 2021), and are a vital component of the marine ecosystem, forming the basis of the marine food web, and acting as a significant sink of carbon dioxide (CO_2) (Tweddle et al., 2018). The abundance and growth rate of phytoplankton blooms are controlled by a complex interplay of factors such as nutrient and light availability, water temperature, and grazing pressure, which makes their global distribution highly heterogeneous (Ibarbalz et al., 2019; Righetti et al., 2019; Bazzani et al., 2023). While macronutrients such as nitrate, phosphate, and silicate broadly constrain productivity in many regions, micronutrients also exert a strong control (Martin et al., 1990; Sunda, 2012). Iron (Fe) is a key micronutrient required by phytoplankton for photosynthesis and for enzymes involved in growth and nutrient uptake, with Fe limitation capping phytoplankton growth even when light and other nutrients are abundant (Browning et al., 2023). Fe concentrations are low in many surface ocean waters (de Baar & de Jong, 2001) due to low solubility in oxygen-rich waters,

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low atmospheric deposition rates, limited upwelling of Fe-rich waters, high rates of scavenging, and the distance from terrestrial input sources (Pollard et al., 2006; Venables & Moore, 2010; Henley et al., 2020; Lauderdale et al., 2020). Past observations and experiments have shown the significant impacts that atmospheric sources such as episodic dust input events can have on Fe limitation, and thus phytoplankton productivity and community structure, despite dust having a low solubility (e.g., Wyatt et al., 2023). While other sources of atmospheric Fe with higher bioavailability than mineral dust, such as biomass burning, are increasingly being studied due to recent severe bushfires (e.g., Winton et al., 2016; Weis et al., 2022), little attention has been paid to extensive volcanic ashfall on the ocean until very recently (e.g., Sánchez-España et al., 2023; Zhang et al., 2024; Chow et al., 2025; Elliott et al., 2025).

Explosive volcanic eruptions produce large volumes of gas and ash which are injected directly into the stratosphere, resulting in impacts on the whole Earth system including terrestrial landscapes, atmospheric dynamics, and oceans (e.g., Manville & Wilson, 2004; Self & Blake, 2008; Self, 2015; Ming et al., 2020; Osipov et al., 2021; Piva, 2023; Wilkinson, 2024). Ashfall is the most widely deposited volcanic product, capable of being dispersed over thousands of kilometres from source, depending on eruption size and atmospheric conditions, with widespread associated environmental impacts (Scasso et al., 1994; Jenkins et al., 2015; Cashman & Rust, 2020). Locally, the deposition of ash on land can result in changes in the physical, chemical and biological properties of soils (Mihai et al., 2023). Further from source, ash dispersal can cover continental-scale areas (e.g., Self, 2015) or spread across vast oceanic regions where it settles onto seawater and eventually the seafloor (Fig. 1). Given the relatively high total Fe content of volcanic ash, the volume of aerosols produced from explosive eruptions, and the spatially widespread influence of eruptions, volcanic ash has the potential to supply micronutrients to large ocean areas. Indeed, several well-documented historic eruptions such as the 2010 Eyjafjallajökull (Iceland) eruptions, and the 2008 Kasatochi eruption (Aleutian Islands) have shown that periodic ashfall over the ocean can influence phytoplankton productivity (Hamme et al., 2010; Achterberg et al., 2013).

Various methods have been used to investigate the links between volcanic ash deposition on the ocean and increased marine primary productivity, including:

1) In situ measurements of chlorophyll (a proxy for phytoplankton biomass) in seawater samples taken by research cruises (e.g., Hamme et al., 2010; Achterberg et al., 2013; Zhang et al., 2024);
2) Lab-based experiments simulating leaching of bioavailable trace metals from ash to seawater (e.g., Frogner et al., 2001; Olgun et al., 2011; Hoffmann et al., 2012; Olgun et al., 2013; Browning et al., 2014; Simonella et al., 2015; Elliott et al., 2025);
3) Biogeochemical ocean modelling and statistical approaches

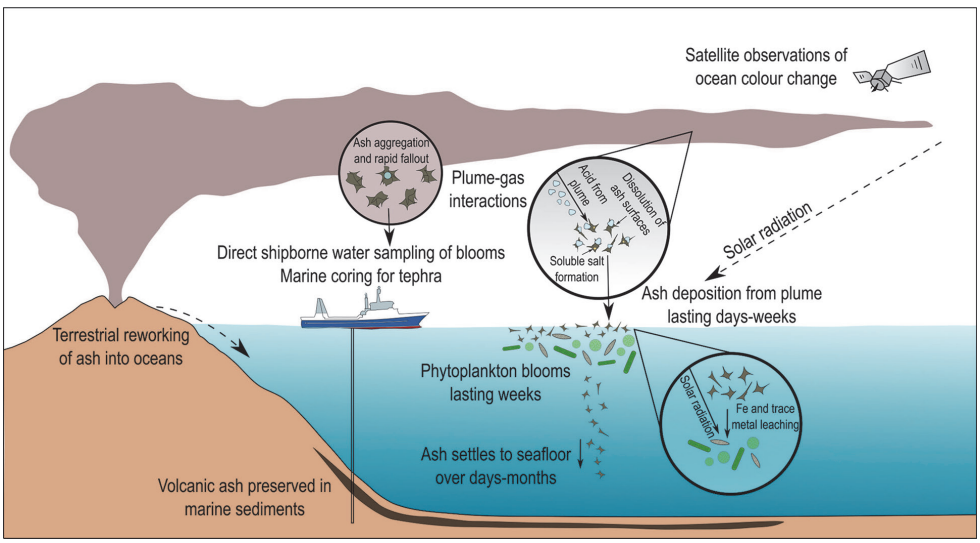

Fig. 1. Schematic diagram showing post-eruption impacts of volcanic ash deposition on phytoplankton populations in the surface ocean.

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(e.g., Lindenthal et al., 2013; Longman et al., 2022; Chow et al., 2025);

4) Satellite observations of ocean colour change, used as a proxy for chlorophyll (e.g., Duggen et al., 2007; Langmann et al., 2010; Lin et al., 2011; Mantas et al., 2011; Westberry et al., 2019).

Due to logistical issues and the unpredictable nature of eruptions, an important data type is rare: in situ measurements (Hamilton et al., 2022). Additionally, the range of eruptions investigated historically are small in magnitude compared to the most explosive eruptions identified in the geological record, including caldera-forming events. A knowledge gap therefore exists around the potential impacts of the largest volcanic eruptions on marine primary productivity.

In this review, we evaluate methods used to assess the severity and timescales of phytoplankton responses to volcanic eruptions, including satellite data and bottle-scale incubation experiments, along with their limitations, to assess knowledge gaps. We examine case studies and the processes by which volcanic ash influences marine biogeochemistry, with a particular focus on phytoplankton productivity. Finally, we propose novel future approaches for studying the marine biogeochemical impacts of large eruptions preserved in the geological record using high temporal resolution ice cores.

2. Drivers of marine phytoplankton productivity

Before considering the impacts of volcanic ash on marine phytoplankton productivity, it is important to highlight that productivity is highly variable across different regions of the ocean. Phytoplankton growth in the oceans is highly sensitive, and can vary in response to seasonal or environmental changes in ambient conditions and nutrient levels (e.g., Martin et al., 1990; de Baar et al., 2005; Cloern et al., 2017; Sundararaman & Shanmugam, 2024). Below we describe the main drivers controlling marine productivity in the distinct oceanographic regions.

2−1 Nutrient availability

Nutrient input to the oceans is one of the key drivers of marine productivity, and can be divided into macro- and micronutrients. Macronutrients such as carbon, nitrogen, phosphorus, and silicon (for diatoms and silicoflagellates) are incorporated into phytoplankton during growth to construct cellular organic matter, and are present in much higher abundance than micronutrients (Hollister et al., 2020). However, trace metal micronutrients are also essential for phytoplankton metabolism, growth, and reproduction, as they serve critical roles in enzyme function, photosynthetic electron transport, respiration, nitrogen fixation, and other cellular processes (Sunda, 2012).

Different oceanographic regions have different ambient nutrient levels which impact baseline productivity (Fig. 2a). High-nutrient, low-chlorophyll (HNLC) regions of the ocean (such as the Southern Ocean) are areas where macronutrients such as nitrate, phosphate, and silicic acid are abundant, and yet primary productivity remains low (Martin et al., 1990; Henley et al., 2020; Bazzani et al., 2023). This phenomenon is largely attributed to the limitation of essential micronutrients, particularly Fe (Fig. 2b), which are required for phytoplankton growth (Martin & Gordon, 1988; Martin et al., 1990). In contrast, low-nutrient, low-chlorophyll (LNLC) regions (such as the North Atlantic gyre) have such low baseline nutrient levels that periodic Fe input often does not trigger the same rapid biological response seen in HNLC areas, highlighting the central role of Fe as a limiting micronutrient in HNLC oceans (Duggen et al., 2010).

Within phytoplankton, Fe supports multiple functions, including alleviating the effects of limited light levels by increasing the concentrations of photosynthetic pigments, reaction centres, electron transport proteins, and protein complexes (Raven, 1990; Sunda, 2012). Fe is also vital for carbon and nitrogen fixation, processes that require high cellular Fe concentrations (Kustka et al., 2003). Other trace metals, while generally required in smaller amounts, can also influence phytoplankton growth and community composition. For example, Mn is important in specific limited regions such as the subarctic Pacific and Southern Ocean, Zn is needed in key proteins for cell growth, and Cu is required in small quantities to assist with Fe uptake (da Silva & Williams, 1991).

In contrast, certain elements can become toxic to phytoplankton when present at high concentrations (e.g., Mann et al., 2002; Echeveste et al., 2012). Toxicity is determined by the amount of free, uncomplexed metal available, rather than the total elemental concentration (Sunda & Huntsman, 1998). Metals such as Cu, Cd, and Zn, while essential in small amounts, can displace other nutrients from their active sites within proteins, hindering productivity (Hartwig, 2004; Valko et al., 2005). Cu is often regarded as one of the main toxic elements for phytoplankton, with incubation experiments showing negative effects on phytoplankton from desert dust-derived sources (Paytan et al., 2009). Overall, the metabolic requirements of phytoplankton depend on a fine balance

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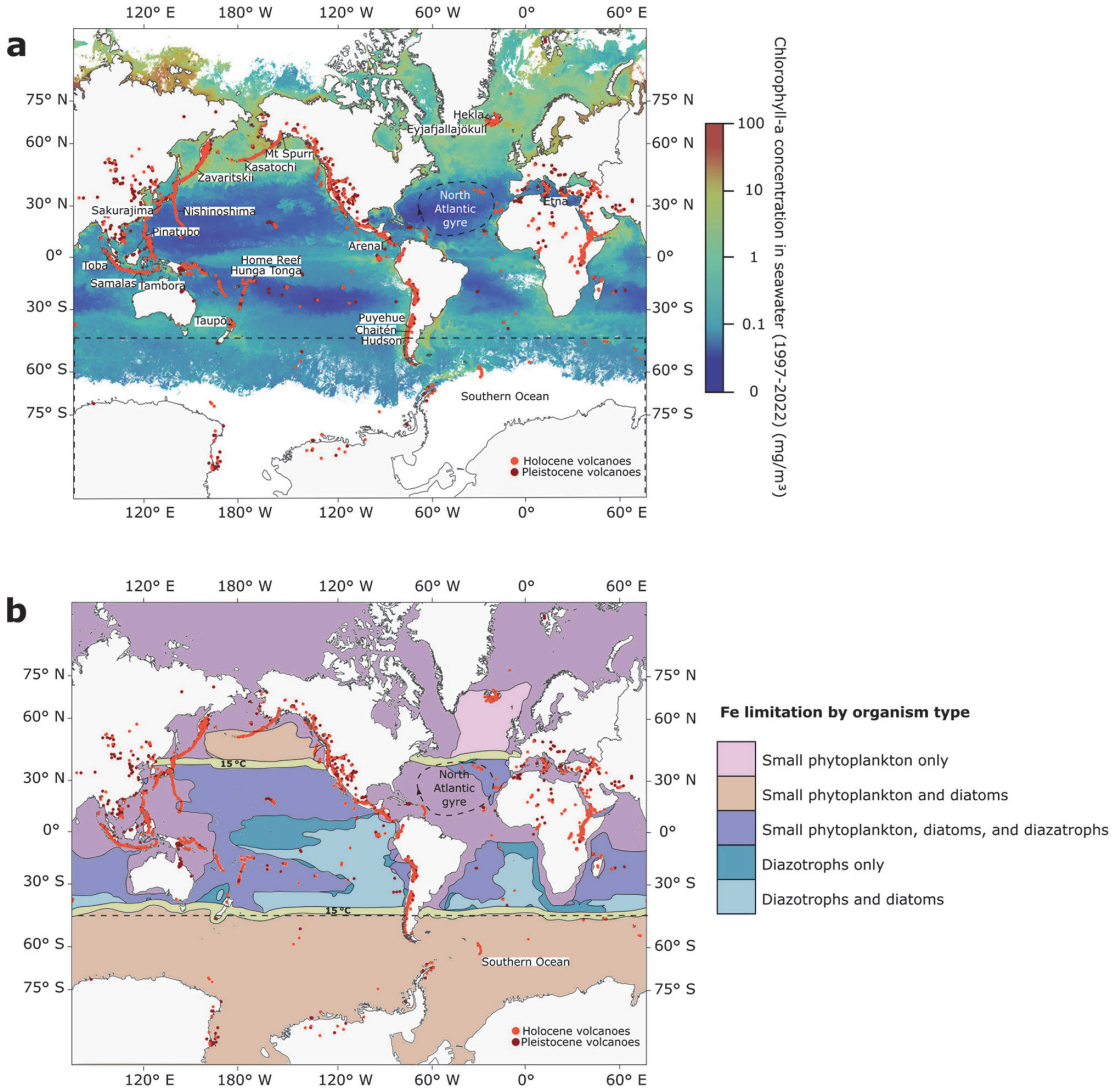

Fig. 2. a) Monthly chlorophyll-*a* concentration in seawater from 1997−2022, alongside a map of global volcanoes active in the Holocene (orange dots) and Pleistocene (red dots). Examples of HNLC (Southern Ocean) and LNLC (North Atlantic gyre) ocean regions are labelled. Chlorophyll-a dataset: Sathyendranath (2023) (last accessed on 23−07−2025). Global volcanoes: GVP (2025). (last accessed on 16−07−2025). Basemap: QGIS (2025). b) Regions of iron limitation in the ocean for small phytoplankton, diatoms, and diazatrophs, after Mahowald et al. (2018).

between trace metal concentrations that are sufficient for growth and those that reach toxic levels. The introduction of additional trace metal sources (e.g., dust or ash) into a marine system has potentially to disrupt these cellular processes in both positive and negative ways. Interactions between trace metals, macronutrients, and phytoplankton are highly complex; trace metal concentrations shape both productivity and community structure, while phytoplankton activity, in turn, influences the cycling and chemistry of these nutrients in ocean waters (Sunda, 2012).

Here, we focus on Fe as the most important limiting micronutrient. Sources of Fe to the surface ocean include atmospheric Fe (mineral dust, biomass burning, volcanic ash), upwelling of Fe rich benthic waters, hydrothermal vents, resuspension of continental shelf sediments, riverine runoff, and melt from icebergs and sea ice that release Fe originally deposited as dust (Moore et al., 2001; Ludwig et al., 2009; Tang et al., 2021; Weis et al., 2022).

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It is not the total amount of Fe present that is important to phytoplankton, but the amount that is soluble or bioavailable, which is operationally defined as Fe <0.2 µm (dissolved Fe; dFe). Fe solubility of particles is controlled by a number of factors including particle size, mineralogy, and atmospheric processing (Baker & Croot, 2010). The solubility of Fe derived from mineral dust is typically low (dFe <1 %), meaning that only a small proportion dissolves in seawater and becomes bioavailable (e.g., Winton et al., 2015).

In the Southern Ocean, the concentration and fractional Fe solubility (the portion of Fe that is able to dissolve in water, and therefore is available to phytoplankton) of dust-derived Fe is considered the primary limitation for phytoplankton growth (Henley et al., 2020; Winton et al., 2022). Measurements from biomass burning in northern Australia have shown that these pyrogenic particles have higher fractional Fe solubilities than dust, ranging from 2−12 % (Winton et al., 2024). This is due to both the greater surface area-to-volume ratio of the particles, and atmospheric processing during transport, highlighting the potential for biomass burning events to produce bioavailable Fe (Ito et al., 2019). The recent 2019/2020 Australian wildfires and dust storm events also ejected an unprecedented mass of biomass burning aerosol and mineral dust to the Southern Ocean, which triggered phytoplankton blooms lasting up to nine months in duration after initial deposition through Fe recycling and ongoing atmospheric supply (Tang et al., 2021; Weis et al., 2022; Winton et al., 2024). In addition to dust and biomass burning aerosol, episodic deposition of volcanic ash also represents an important, yet largely unconstrained, source of atmospheric trace metals which can stimulate phytoplankton blooms (e.g., Hamme et al., 2010; Achterberg et al., 2013) (Figs. 1 & 2). Ash input can vary over orders of magnitude, with long-term fluxes being skewed by the largest eruptions (Galetto et al., 2023).

2−2 Environmental conditions

Sufficient nutrient availability can only trigger a phytoplankton bloom when light levels are also favourable, as light is required for photosynthesis. Seasonal changes in light availability therefore play a crucial role in influencing the timing and magnitude of marine phytoplankton growth in global oceans.

During the long polar winter, 24-hour darkness and the onset of deep ocean mixing prevents phytoplankton growth. Many species respond by altering their metabolism and forming “resting stages” that sink to the seafloor or become trapped in sea ice (Johnsen et al., 2020). In spring, the return of sunlight causes greater stratification in the surface ocean, leading to a shallower mixed layer - a surface ocean zone where the atmosphere and ocean interact through the exchange of heat and gases (Arteaga et al., 2020). This, along with the release of phytoplankton from their resting stages, results in spring blooms (Kauko et al., 2021). In temperate regions, blooms also occur in spring as surface waters warm, sunlight for photosynthesis increases, and terrestrial runoff delivers additional nutrients (Rumyantseva et al., 2019). Cool ocean temperatures during this period have been suggested to result in slowed grazer development rates compared to phytoplankton, which means phytoplankton can temporarily outgrow grazers and form large blooms for a short period (Irigoien et al., 2005; Rose & Caron, 2007; Diehl et al., 2022). By contrast, tropical oceans are generally nutrient-limited, resulting in low productivity. In these regions, phytoplankton growth is more strongly influenced by upwelling and monsoon cycles than by seasonal light variation (e.g., Naik et al., 2020).

In polar and temperate regions, rising air temperatures during spring and summer increase SSTs. These elevated temperatures, together with increased nutrient availability, enhance the light-harvesting capacity of phytoplankton and help to promote blooms (Fernández-González et al., 2022). In tropical regions, temperature is less variable annually, and is not a major limiting factor for primary productivity. Phytoplankton species have optimal SST ranges in which their growth rates are at their peak, often reached during the spring and summer growth seasons; however, SSTs exceeding these limits may hinder their productivity (Boyd et al., 2013). In the context of volcanic ashfall, seasonality could play a significant role in determining the way in which different phytoplankton species respond to a sudden influx of nutrients.

3. Volcanic ash impacts on the ocean

3−1 Volcanic ash generation and properties

Volcanic ash is fine-grained (<2 mm) material produced by the fragmentation of magma during explosive volcanic eruptions. Ash generation can result from several mechanisms, including rapid decompression, expansion of gas bubbles, shear failure, mechanical abrasion in the plume and the interaction of magma with external water (Mader et al., 1994; Duggen et al., 2010; Dingwell et al., 2012; Paredes-Mariño et al., 2022). Ash is then injected into the atmosphere either directly through high-temperature, buoyant eruption plumes, or via elutriation of ash from PDCs prior to transport (Cashman & Rust, 2016; Jones et al., 2023).

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Volcanic ash deposition on the ocean represents a sudden environmental change that can perturb ocean chemistry and subsequently impact ocean dynamics and marine life (e.g., Hamme et al., 2010; Achterberg et al., 2013). The properties of volcanic ash are important for determining the specific biological responses in the ocean. Ash contains a variety of bioavailable chemical constituents that are limiting micronutrients in the ocean, including Fe, Co, Zn, and Mn, and macronutrients such as P, Si, and Mg (Browning et al., 2015; Simonella et al., 2015; Schoffman et al., 2016; Bisson et al., 2023). However, ash may also release potentially toxic metals including Cd, Cu, Pb, and Zn, which can adversely affect marine primary productivity (Hoffmann et al., 2012). Therefore, many uncertainties remain around how volcanic ash may enhance or limit phytoplankton bloom growth or decay (Bisson et al., 2023). There also remains a significant knowledge gap around the interaction of multiple trace metals within marine systems. In particular, the relative ratios of micronutrients may strongly influence phytoplankton community structure. While macronutrients are known to affect these communities (e.g., Dolman et al., 2012; Hofmann et al., 2019), certain metal ratios could also favour specific phytoplankton groups based on their metabolic needs.

Volcanic ash particles have varied properties, including their chemical composition, size, and the morphology of glass shards, all of which variably impact the leaching of bioavailable elements into the ocean (Bisson et al., 2023). Mafic magmas (basaltic to andesitic) typically contain higher amounts of Fe and compatible biologically-relevant trace metals. However, the grainsize distribution of ash particles may be important for determining Fe solubility in seawater (Simonella et al., 2015). Fine-grained volcanic ashes have higher specific surface area, which is a key factor that can increase their solubility in sea water, potentially allowing more extensive chemical leaching than larger ash particles (Simonella et al., 2015). On the other hand, Elliott et al. (2025) note that particle size did not appear to be a primary control on Fe release in their study, with acidic processing in the atmosphere playing a more significant role.

Ash particle sizes vary widely depending on magma composition, eruption style, and eruption magnitude. For example, silicic eruptions (i.e., dacite to rhyolite) typically produce finer ash particles due to their high volatile content and viscosity, which leads to explosive and efficient fragmentation (Langmann, 2013). Rose and Durant (2009) suggest that basaltic eruptions produce only about 1–4 % very fine ash (<30 μm), whereas rhyolitic eruptions can generate 30 % to over 50 %. Silicic eruptions can also generate large-scale pyroclastic flows, which further contribute to the secondary production of fine ash through abrasion (Rose & Durant, 2009). Although magma composition often plays a key role in determining grainsize, there are exceptions. For example, basaltic Plinian eruptions can still generate relatively fine-grained ash due to rapid decompression. In addition, phreatomagmatic eruptions triggered by explosive interactions between magma and water may also produce fine-grained ash, although dispersal is not as widespread (Langmann, 2013), likely because increased moisture and salt availability in the plume promotes rapid aggregation and fallout (Colombier et al., 2019).

The distribution and environmental impacts of volcanic ash depends not only on its grainsize and composition, but also on how it is subsequently transported through the atmosphere to the water column. Depending on eruption size and wind direction, airborne ash can disperse and settle out over large areas of ocean where it falls onto the sea surface and percolates through the water column. Ash produced by subaerial volcanic eruptions can be transported in volcanic plumes at elevations that can exceed 50 km height in the most explosive (Plinian to Subplinian) events (e.g., Proud et al., 2022). Stratospheric-level transport and fine grainsize means that ash from these events can travel hundreds to thousands of kilometres from vent (Fig. 3), with progressive fining with distance increasing particle surface-to-volume ratios, and consequently increased reactivity upon deposition (e.g., Cashman & Rust, 2016). Lower intensity eruptions that generate lower-level plumes have more restricted ash distribution, but high winds can still transport small quantities of ash over thousands of kilometres, as demonstrated by numerous historic events (e.g., 2010 Eyjafjallajökull (Iceland) eruptions (Achterberg et al., 2013)). Submarine eruptions can also produce large ash plumes; however, water interaction may restrict plume development and result in more localised injections of ash into the water column (e.g., the 2012 Havre submarine eruption, Kermadec arc; Ikegami et al. (2018); Murch et al. (2024)). Submarine volcanism (e.g., Duggen et al., 2007; Wilson et al., 2019; Barone et al., 2022; Bonnet et al., 2025) and hydrothermal vents (e.g., Ardyna et al., 2019; Schine et al., 2021) are important sources dissolved iron to the ocean and have been shown to trigger large phytoplankton blooms globally, although not all submarine volcanoes trigger phytoplankton blooms (e.g., Gómez-Letona et al., 2018).

Given the proximal location of many global volcanoes to oceans due to their formation via oceanic plate subduction at

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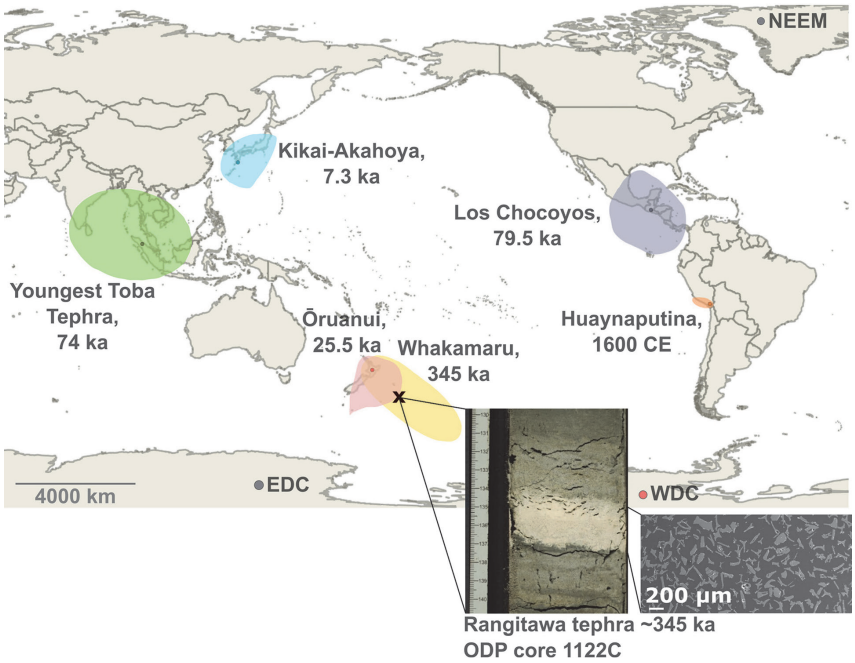

Fig. 3. Map showing a selection of large volcanic eruptions and their associated ash coverage as estimated from visible macro-tephra deposits from marine cores and terrestrial deposits, demonstrating the minimum distance of extensive ash deposition. It should be noted that trace or cryptotephra deposits likely extend much further across large oceanic regions. For example, glass shards from the Ōruanui and Los Chocoyos eruptions have been discovered in Antarctica in the WDC and EDC cores respectively (Dunbar et al., 2017; Innes et al., 2025), and Los Chocoyos glass has also been identified in the NEEM ice core in Greenland (Innes et al., 2025). The 'X' symbol shows the location of marine core ODP 1122C, where an example of a macrotephra deposit from the Whakamaru eruption is shown. Isopach data from: Matthews et al. (2012); Alloway et al. (2013); Vandergoes et al. (2013); Kutterolf et al. (2016); Mariño et al. (2021); Hamada et al. (2023). Marine core image of the Rangitawa tephra from IODP (Carter et al., 1999; IODP, 2025). Electron microprobe image of Rangitawa tephra from Anna Miller. World basemap: QGIS (2025).

convergent margins (Fig. 2), volcanic ash is a major source of particulate delivery that carries a range of chemicals that can potentially impact on marine life. Ash layers from large explosive eruptions are often preserved in the geological record as distinct tephra layers in marine sediments that can exceed tens of centimetres in the largest and most explosive events, highlighting the widespread dispersal of ash during past eruptions (Fig. 3). For example, thick layers of the 79 ka Youngest Toba Tuff (YTT) are found in marine cores across the Indian Ocean (Kutterolf et al., 2023). The 1 cm isopach for this eruption covered a minimum area of 3.8×10^7 km^2 with an erupted tephra volume of ~2600 km^3. Multiple supereruptions from the central Taupō Volcanic Zone (TVZ) in New Zealand have ejected huge volumes of ash across the Southern Ocean. In particular, the 345 ka Rangitawa Tephra occurs in marine cores thousands of kilometres from mainland New Zealand as a distinctive white lens within deep sea marine sediments (Fig. 3) (Matthews et al., 2012; Miller et al., 2026). Marine tephras display a wide variety of appearances depending on sediment substrate and if the deposit has been reworked on the seafloor (Gudmundsdóttir et al., 2011; Freundt et al., 2023). As such, it is challenging to relate the amount of ash in marine cores to the amount of ash that would have been deposited on the surface at the time of eruption. However, tephras in deep marine settings with low sedimentation rates suggest that in many cases, marine tephras provide a minimum estimate. In contrast, tephras in closer proximity to the mainland or down slopes may be subjected to significant reworking and overthickening (Gudmundsdóttir et al., 2011; Hopkins et al., 2020).

3−2 Ash-derived nutrient delivery to the ocean

The mechanism of ash deposition to the surface ocean can influence the timing and nature of the marine biogeochemical impacts. Dry deposition from the volcanic plume occurs when ash particles settle under the influence of gravity, whereas wet

deposition involves scavenging of particles by moisture and aggregation (Bisson et al., 2023). Coarser particles tend to settle more rapidly and closer to vent due to their greater mass, whereas fine particles can be transported hundreds to thousands of kilometres from vent across vast areas of the ocean (Figs. 1 & 3). One important process is plume scrubbing, where volcanic gases and ash interact with atmospheric moisture, forming acidic precipitation which scavenges ash particles from the plume (Manzella et al., 2015; Van Eaton et al., 2015; Mueller et al., 2017). In wet atmospheric conditions, particles of ash clump together to form larger aggregates, or can aggregate around ice nuclei, causing them to settle out more rapidly (Brown et al., 2012). Volcanic plumes are the most efficient way to transport large amounts of volcanic ash across vast regions of the ocean, however ash deposits can also be remobilised from terrestrial deposits for months or years after eruptions.

The timing and nature of ash deposition, whether directly deposited from the plume or remobilised from land, affects the extent of salt leaching and nutrient release. Fresh ash deposited directly from the eruption plume can be coated with soluble salts that dissolve readily when in contact with water, releasing a range of cations that can lead to changes in water chemistry and local nutrient levels (Jones & Gislason, 2008; Mueller et al., 2017; Stewart et al., 2020). Depending on length of transport and atmospheric conditions, hydrous acids and brines coating ash surfaces can generate the greatest leachate upon deposition, exceeding contributions from the ash itself (Jones & Gislason, 2008). In contrast, ash that is remobilised by wind or water after settling on land would have already undergone leaching and weathering, removing soluble components and reducing nutrient release (Witham et al., 2005; Browning et al., 2015; Bisson et al., 2023).

Once ash is deposited on the surface ocean, its behaviour and environmental effects depend on a range of factors. The density, buoyancy, and solubility of ash particles on the sea surface play a crucial role in the leaching of bioavailable elements. Oceanographic conditions also play a role, as sea water chemistry, and circulation and mixing patterns can influence the residence time of ash in the surface layer (Zhang et al., 2024), while the biological response is also shaped by the ambient oceanographic conditions including nutrient and chlorophyll concentrations.

3−3 Soluble Fe leaching from volcanic ash

As with established work on mineral dust and biomass burning aerosols, the solubility of trace metals is a key factor in determining the fertilisation potential of volcanic ash. Among trace elements, the concentration and fractional solubility of Fe is often considered the most critical driver of marine microbial growth (Henley et al., 2020; Winton et al., 2022). While the total Fe content of glass is relatively high, it varies greatly for different magma types, from high concentrations in mafic compositions (i.e., typically >3−5 wt.% in basalts to andesites), to lower levels in more evolved silicic melts (i.e., <1−2 wt.% dacite to rhyolite). However, the bioavailability of Fe from volcanic ash remains poorly constrained. The only current estimate suggests that Fe in volcanic ash has a fractional solubility of < 6 % (Elliott et al., 2025).

The solubility of Fe in ash can vary widely depending on specific ash composition. Ayris and Delmelle (2012) previously established that assuming a typical Fe content in ash of 2−8 %, Fe solubility may form a much lower range, between <0.01−0.1 %, although some ash specimens they recorded were up to ~1 %. Studies of fresh volcanic ash from a large number of eruptive sources suggest that, in seawater with low Fe concentrations, soluble Fe leached from ash ranges between 35 and 340 nmol g^{-1} of ash (Olgun et al., 2011). This finding is broadly supported by detailed investigations of individual ash samples (e.g., Duggen et al., 2007; Olgun et al., 2011; Olgun et al., 2013).

The amount of soluble Fe also depends on grainsize and the surface area of the ash exposed to leaching. Witham et al. (2005) showed that leachates from a range of different composition ash samples varied in Fe content over several orders of magnitude between 0.0004−3.64 mg L^{-1}. Furthermore, in their investigation of ash deposited in seawater from eruptions of the southern Andes, Simonella et al. (2015) suggest that despite lower glass Fe contents, Fe solubility is higher in ash of rhyolitic composition compared to andesitic composition because of finer grainsize. It should also be noted that while volcanic ash deposition is an important source of Fe in the surface ocean, ash can also act as a sink of Fe through adsorption (Rogan et al., 2016). Although few studies have examined this in the context of volcanic ash, research on dust deposition suggests similar effects (e.g., Johnson et al., 1997; Wagener et al., 2010; Ye & Völker, 2017). Wagener et al. (2010) reported that large dust deposition events can reduce surface-ocean dissolved Fe, potentially due to dust particles scavenging significant quantities of Fe during sinking. This mechanism may also apply to ash; however, investigations of this scavenging process are still limited (Baker & Croot, 2010).

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3-4 Enhancement of Fe solubility in volcanic plumes

Atmospheric processing can enhance Fe solubility, a phenomenon that has been observed previously during long-range transport of particles, particularly in air masses containing high amounts of acidic, polluted, or pyrogenic aerosols (e.g., Chen & Siefert, 2004; Hand et al., 2004; Ito & Shi, 2016; Li et al., 2017; Baldo et al., 2022; Perron et al., 2022; Winton et al., 2022). Enhancement through cloud processing, organic complexation, or photochemical reactions may subsequently influence impacts on distal ocean regions (Shi et al., 2011; Ito et al., 2019; Weis et al., 2022). Particle-gas interactions within acidic volcanic plumes containing hydrofluoric (HF) and sulfuric acid can also substantially increase Fe solubility. This can occur through acid-driven dissolution of ash particle surfaces (Wolff-Boenisch et al., 2004; Delmelle et al., 2007; Hoshyaripour et al., 2015; Elliott et al., 2025), or changes in the Fe oxidation state of volcanic glass (Mueller et al., 2017; Wadsworth et al., 2021). Eruptions with high quantities of sulfuric gases and halogens promote the formation of strong acids, which can alter ash within the plume and release readily soluble, biologically-relevant trace elements and salts that can dominate rapid leaching in the ocean's mixed layer (Jones & Gislason, 2008; Ayris & Delmelle, 2012; Mueller et al., 2017). Sulfate, fluorine, and chlorine are all preferentially enriched on ash surfaces (Delmelle et al., 2000; Delmelle et al., 2007), with fluorine in particular exerting a strong control on ash dissolution (Wolff-Boenisch et al., 2004; Jones & Gislason, 2008). When converted to HF acid, it efficiently dissolves aluminosilicates, promoting bulk dissolution of the ash surface layer (Jones & Gislason, 2008; Delmelle et al., 2021). For example, analyses of Tajogaite ash (La Palma, Canary Islands) reveal exceptionally high Fe mobilisation was likely driven by F-enriched surface salts formed during plume-gas interactions (Sánchez-España et al., 2023). Sulfuric gases in the plume also influence ash by promoting reactions that lead to sulfate salt formation and increased ash surface reactivity (Wadsworth et al., 2021).

The oxidation state of Fe is also critical to its bioavailability. Elliott et al. (2025) noted that Fe hosted within silicate rather than oxide phases in ash was more soluble in seawater, with other studies noting the solubility in silicates also depends on the structural position of Fe within the mineral lattice (Brantley & Chen, 1995; Jones & Gislason, 2008). When Fe is incorporated in halide form and adsorbed onto ash surfaces, it is readily soluble due to lower crystal lattice energies and more favourable interactions with water molecules. Together, these observations suggest that plume gas composition and atmospheric processing history exert the dominant controls volcanic ash Fe solubility and its potential to stimulate phytoplankton productivity (Elliott et al., 2025).

4. Potential impacts of ash deposition to the ocean and primary productivity: methods of investigation and case studies

Despite growing recognition of the potential importance of ash deposition to ocean ecosystems, direct observations remain rare. Most understanding comes from laboratory experiments and satellite observations rather than field-based studies conducted during or immediately after eruptions. This is due to the unpredictable nature of eruptions and the logistical challenges of rapid deployment of research vessels to remote ocean regions. Nevertheless, some experimental studies have used in situ seawater and fresh ash from historic eruptions in their investigations as further considered below.

4-1 In situ measurements of ash deposition

Only a handful of studies have captured immediate biological responses to ash deposition at sea. One such study by Hamme et al. (2010) examined the impact of the 2008 Kasatochi eruption from the Aleutian Islands, Alaska, which deposited ash over wide areas of the subarctic northeast Pacific. Direct chlorophyll-*a* measurements taken by filtering seawater samples during two oceanographic cruises and analysing them fluorometrically revealed that discrete surface chlorophyll concentrations west of 130° W were twice the average expected for that time of year. These findings aligned well with satellite observations recorded over the same period, indicating a high-productivity event caused by Fe fertilisation from volcanic ash. A more recent study investigated Fe fertilisation of phytoplankton blooms in the Iceland Basin of the North Atlantic following the 2010 Eyjafjallajökull eruption (Achterberg et al., 2013). Shipboard measurements taken beneath the ash plume by three research cruises showed significantly elevated dissolved Fe concentrations in surface waters. These findings were supported by lab-based experiments on freshly collected ash, which indicated high potential of the Eyjafjallajökull ash to enhance phytoplankton growth through Fe fertilisation.

In situ studies have confirmed that ash deposition has the potential to rapidly stimulate phytoplankton blooms. However, each study assesses impacts differently, using varied instruments, sampling methods, and analytical approaches, which makes it

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difficult to corroborate findings across studies. This highlights the need for more standardised investigations into the immediate, direct responses of phytoplankton to volcanic ash deposition. An ongoing limitation of direct observations is that eruptions and ash deposition are impossible to predict in advance to allow for cruise planning and sample collection. For such logistical reasons, it is likely that although direct observations are vital for our understanding, they will remain rare and opportunistic.

4−2 Experimental studies

Laboratory experiments have demonstrated that volcanic ash is capable of releasing significant amounts of biologically-relevant nutrients, suggesting a strong potential impact on marine primary productivity (e.g., Olgun et al., 2011; Hoffmann et al., 2012; Olgun et al., 2013; Browning et al., 2014; Mélançon et al., 2014; Simonella et al., 2015, and references therein). Experimental studies offer unique insights into the reaction between volcanic ash and seawater and the potential effects of ash-derived metals and toxins on marine organisms. Incubation experiments simulate volcanic ash deposition under seawater conditions to assess its effects on natural phytoplankton communities by comparing ash-treated samples with controls. In contrast, leaching experiments focus only on quantifying the amount of macro- or micronutrients released from specific ashes.

4−2−1 Leaching experiments

An early study by Frogner et al. (2001) exposed ash from the 1991 Hekla eruption (Iceland) to seawater and determined multiple phytoplankton-relevant nutrients (including Fe, P, and Si) were released within hours. This was the first study to suggest that the deposition of volcanic ash in the marine environment may impact on primary productivity. Since this initial work, numerous laboratory-based experiments have been undertaken using ash from a variety of sources, compositions, and leached in different ocean waters (e.g., Duggen et al., 2007; Olgun et al., 2011; Hoffmann et al., 2012; Achterberg et al., 2013; Olgun et al., 2013; Browning et al., 2014; Mélançon et al., 2014; Simonella et al., 2015; Zhang et al., 2024, and references therein), suggesting that surface ocean Fe fertilisation from volcanic ash has high potential to impact marine primary productivity.

Olgun et al. (2011) conducted a similar experiment using a larger sample set of 44 unhydrated ashes. They found that rapid mobilisation of soluble Fe ranged between 35 and 340 nmol/g, with a global average of 200 ± 50 nmol/g. This value is comparable to the soluble Fe released from desert dust under similar seawater conditions (Spokes & Liss, 1996; Guieu et al., 2010). The authors also demonstrated that the volume of ash input to the Pacific Ocean per kiloyear is on the same order of magnitude as the mineral dust input over the same time period, suggesting that volcanic ash is an important yet understudied source of nutrients to global oceans.

A number of other specific case studies on single eruptive events have been conducted since, with one in particular focussing on the 2001−2007 Etna eruptions (Olgun et al., 2013). Seawater leaching experiments using ash from these eruptions assessed potential impacts on marine primary production in the nutrient-poor Mediterranean. Consistent with previous findings, nutrient release occurred within minutes to hours of leaching, releasing substantial amounts of macronutrients (fixed N: 35−855 nmol/g ash; P: 7−970 nmol/g; Si: 3−2060 nmol/g) and micronutrients (Fe: 10−130 nmol/g; Zn: <21 nmol/g), indicating that Etna eruptions is able to supply a significant source of nutrients to the Mediterranean Sea.

Other studies have further explored the role of ash composition and Fe leaching. Simonella et al. (2015) investigated Patagonian ashes from the Chaitén 2008, Hudson 1991 and Puyehue 2011 eruptions in seawater samples to evaluate soluble Fe input into the ocean and therefore nutrient supply. The three ashes leached in this experiment had different compositions: andesite (Hudson), trachydacite (Puyehue), and rhyolite (Chaitén). The results highlighted that magma source is probably one of the most important factors controlling the release of trace metals from volcanic ash, as Fe solubility in seawater was higher for the rhyolitic ash and lower in the andesitic ash. However, because rhyolitic ash contains less Fe overall, andesitic ash may sometimes be more likely to trigger a phytoplankton bloom, whereas rhyolitic ash may not always be sufficient. Supporting the importance of source composition, Simonella et al. (2022) examined the fractional solubility of mineral dust derived from Southern South America, the largest dust supplier to the Southern Hemisphere oceans, and found that dust aerosols release Fe at a steady rate in seawater, whereas volcanic aerosols release Fe much more rapidly. Volcanic ash also exhibited a greater total Fe release in seawater than mineral dust.

Recent work by Elliott et al. (2025) compared ash chemistry, ash-gas interactions, and particle size from two recent eruptions: La Soufrière (Saint Vincent and the Grenadines) and Tajogaite (La Palma, Canary Islands). They performed leaching experiments and found that fractional iron solubility in the

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longer-travelled and finer Tajogaite ash was approximately three times higher than in La Soufrière ash (3.6 % compared to 1.3 %). This enhanced solubility is attributed to stronger interaction with acidic, fluorine-rich plume gases during the Tajogaite eruption, which produced acidic surface coatings (such as HF), that are effective at dissolving aluminosilicates in the ash surface layer. These differences help explain why some eruptions trigger a phytoplankton response while others do not, clearly demonstrating the importance of chemical processing in the plume for increasing iron solubility in volcanic ash.

4-2-2 Incubation experiments

The timescale of phytoplankton productivity changes following eruptions has been a key focus of research, often investigated through incubation experiments. Duggen et al. (2007) investigated unhydrated ash from three subduction zone volcanoes: basaltic-andesitic ash from Arenal (Costa Rica), andesitic-dacitic ash from Sakurajima (Japan), and andesitic ash from Mount Spurr (Alaska). Ash was leached in low-metal Antarctic seawater to examine biological response. Within minutes of contact with seawater, ash from all three sources released a suite of nutrients that supported phytoplankton growth, including Fe (10−60 g^{-1} ash within 20 minutes), Zn (2−27 nmol g^{-1}) and Cu (0−50 nmol g^{-1}). This study suggested, for the first time, that subduction zone ash can rapidly supply critical micronutrients that trigger phytoplankton blooms. This effect may partly arise from the sulfur and halogen-rich gas compositions in subduction zone settings, which promote the formation of soluble salt deposits on ash surfaces and enhance Fe bioavailability (Duggen et al., 2007).

Experimental studies have also assessed the possibility that volcanic ash may exert both fertilising and toxic effects on marine phytoplankton. Hoffmann et al. (2012) used laboratory-based experiments to demonstrate for the first time that trace metal release from volcanic ash can have variable impacts on different phytoplankton species. In their study, trace metal release into seawater was stimulated for four different volcanic ashes and quantified relative to the growth rate of reference diatom and coccolithophoride species. Consistent with earlier findings by Olgun et al. (2011), Hoffmann et al. (2012) observed that significant trace metal release occurred within minutes of contact with seawater, indicating that leaching begins immediately following ash deposition, even though larger particles may rapidly sink out of the surface ocean. Mn was also found to elicit some control over phytoplankton growth. The experiment showed that the same volcanic ash can act to both increase and decrease the growth rate of different phytoplankton species, thus the response of marine phytoplankton communities to the input of ash is far more complex than previously suggested and may lead to changes in species composition.

Browning et al. (2014) explored this complex relationship in their bottle enrichment experiment by spiking surface seawater samples collected on cruises in the South Atlantic and Southern Ocean with volcanic ash. Fresh basaltic ash from the Etna 2002 eruption (Sicily) and rhyolitic ash from the Chaitén 2008 eruption (Chile) were both tested for biological response (Fig. 4). Significant phytoplankton growth changes were recorded in most samples, including from sites where the concentration of dissolved Mn in seawater was extremely low, suggesting potentially heightened responses due to the ash providing relief for Mn limitation.

Experiments have also explored how volcanic ash influences changes in phytoplankton taxonomic composition. Using ash collected from the 2008 Kasatochi and Chaitén eruptions, Mélançon et al. (2014) assessed the response of phytoplankton in the Fe-limited subarctic Pacific Ocean. In their study, fresh ash collected after the eruptions during a research cruise was added to seawater samples from various depths in the water column. After a four-day lag period, increases in the carbon fixation rate and chlorophyll-*a* concentrations up to three times were noted. The primary species dominating the incubated phytoplankton population were diatoms, however others including cyanobacteria and dinoflagellates were also seen to be stimulated. This supported the notion that volcanic ash deposition from both eruptions would have been sufficient to trigger phytoplankton blooming, supporting existing satellite observations, and highlighting the importance of episodic ash deposition for stimulating blooms in the North Pacific. It was also demonstrated that not all species were fertilised by the ash to the same extent, another indication that some species can be potentially negatively impacted by ash addition.

Overall, laboratory experiments show that volcanic ash can substantially increase nutrient input to surface oceans, temporarily relieving natural limitations and stimulating phytoplankton blooms, while also introducing potential toxicity and complex species-specific responses. However, these studies also show limitations of experimental methods. Scaling up from experiments on a bottle scale to large areas of ocean has inherent uncertainty associated with it, as controlled laboratory conditions cannot fully replicate the complex

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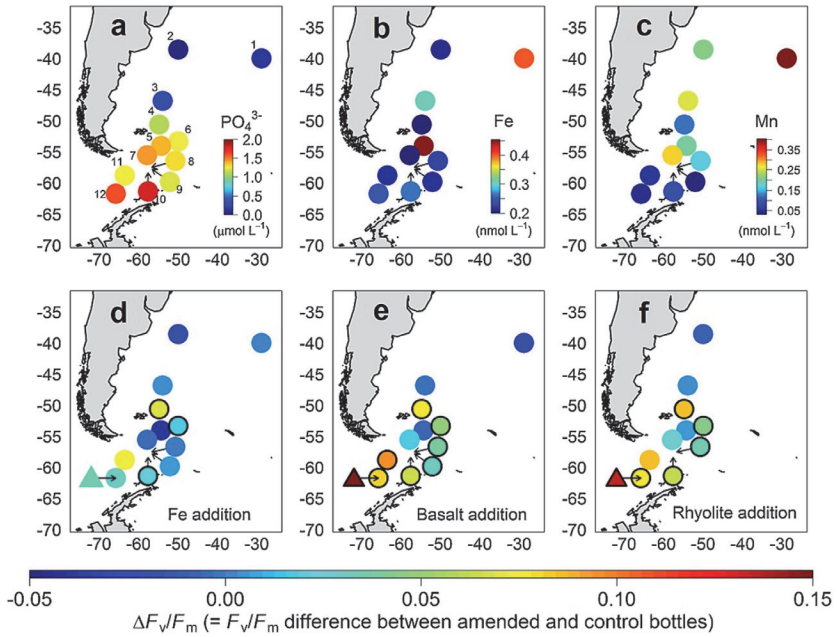

Fig. 4. Nutrient concentrations in seawater samples from the Drake Passage (a-c), and the response of phytoplankton in each case to the addition of Fe and ashes of two different compositions (d-f). Circles represent the response after 24 hours of incubation, and triangles represent the response after 48 hours of incubation. F_v/F_m is defined as apparent photochemical efficiency of energy conversion (i.e. the physiological response of phytoplankton). Figure reprinted from Browning et al. (2014) with permission: https://creativecommons.org/licenses/by/3.0/.

physical, chemical, and biological interactions occurring in the open ocean. For example, in laboratory-based experiments it may not be possible to quantify and replicate light conditions, water temperature, or pre-existing nutrient conditions, all of which impact phytoplankton growth and species composition in the surface ocean. These limitations further highlight the need for more in situ observations to better understand the influence of volcanic ash on ocean biogeochemistry and marine ecosystems.

4-3 Remote sensing of ash impacts on oceans

Remote sensing methods provide global coverage and high temporal resolution data, providing valuable insights into how marine organisms respond to ash deposition, without requiring direct 'real-time' sampling. Satellites can detect minor changes in ocean colour, which is related to the presence of chlorophyll-*a*, a proxy for surface ocean biomass due to it being the main photosynthetic pigment found in phytoplankton (Wilson et al., 2019; Barone et al., 2022; Kelly et al., 2023). Remote sensing observations of ocean colour are important for putting direct observations and lab experiments of ash impacts into context, and satellites have been particularly useful for this purpose as early as 1978 (Langmann et al., 2010).

An early, but well-studied example of remote sensing for this purpose comes from the August 2008 Kasatochi eruption (Aleutian Islands). Satellite data showed a significant increase in chlorophyll-*a* concentration in the Fe-limited northeast Pacific, where most of the ash was deposited (Hamme et al., 2010; Langmann et al., 2010). This increase was notable compared to the average values for the same months in previous years and thought to represent an increase in marine primary productivity due to deposition of volcanic material on the surface ocean (Duggen et al., 2010; Hamme et al., 2010; Langmann et al., 2010). Westberry et al. (2019) also noted potential physiological changes in the phytoplankton community in the wake of the eruption through analysis of the chlorophyll-to-carbon biomass ratio, which can now be retrieved from satellite ocean colour data. These changes included signs of Fe stress relief, changes to growth rates, and increases in biomass in response to ash deposition.

In addition to monitoring chlorophyll-*a* changes during an eruption, satellite observations can detect plumes of discoloured water of volcanic origin. Mantas et al. (2011) used remote sensing data from multiple sensors to analyse the 2006 Home Reef volcano eruption (Tonga), focusing on ocean chlorophyll-

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a concentration (OCC), SST, and discoloured water plumes. They observed anomalies in OCC and identified a large phytoplankton bloom, contributing values up to 17 times higher than the background, associated with an extensive plume of discoloured water.

Combining remote sensing with additional methodologies can also reveal interesting results. Chow et al. (2025) used remote sensing techniques along with in situ sensors to investigate a large phytoplankton bloom following the 2018 Kīlauea (Hawaii) eruption. A lag of approximately one month was observed between ash deposition at the ocean surface and the maximum bloom extent; this delay was attributed to nitrogen limitation and the initially low abundance of nitrogen-fixing diazotrophs. Iron availability, or a combination of iron and phosphorus supplied by volcanic ash, was considered a key factor in stimulating diazotroph growth during the 2018 bloom. The study highlights that the pre-existing nutrient balance and phytoplankton community composition strongly influence whether a bloom develops. In addition, the occurrence of such a large bloom following the low-intensity Kīlauea eruption suggests that fragmentation of ash into fine particles under explosive conditions may not be a major control on iron dissolution or the biogeochemical impact of volcanic ash deposition.

Remote sensing methods have also been found useful for monitoring ongoing eruptions with multiple or complex phases. For example, 8 months of explosive and effusive volcanic activity from Nishinoshima volcano (Japan) in 2019−20, an island in an LNLC oceanic setting in the Northern Pacific, allowed ongoing impacts to be observed through satellite observation during the eruption (Kelly et al., 2023). During effusive, lava-producing eruption phases, no notable changes to chlorophyll-*a* concentration occurred. However, during the explosive phase, recorded concentrations were well above background (Fig. 5). These increases were shown to represent phytoplankton blooms using a sun-induced chlorophyll-*a* fluorescence satellite product, which is a re-emitted spectral signal covering the wavelengths produced by plants absorbing sunlight, and is a proxy for photosynthesis and carbon uptake in organisms. Kelly et al. (2023) also hypothesize that the resulting phytoplankton blooms from the Nishinoshima eruption led to significant (10^{10}-10^{12} g) drawdown of carbon.

More recently, the explosive 2022 Hunga Tonga–Hunga Ha'apai eruption has been the focus of debate over whether it produced a massive phytoplankton bloom. Barone et al. (2022) were the first to report a potential bloom, noting a large area with chlorophyll-*a* concentrations around ten times higher than pre-eruption levels, visible in satellite data less than 48 hours after the largest eruptive phase. However, Whiteside et al. (2023) challenge this interpretation, suggesting that standard ocean-colour algorithms misidentified volcanic ash as phytoplankton, with basaltic-andesitic material on the surface ocean being responsible for the observed satellite signal. Thus, the impacts of the Hunga Tonga–Hunga Ha'apai eruption are still the subject of ongoing research and debate, with further data and publications expected (Mackay et al., 2022).

4−4 Synthesis of methods and case studies

After evaluating existing case studies on the impacts of volcanic ash deposition on phytoplankton productivity and composition, it is evident that there is existing, reliable knowledge of the short-term biological responses, particularly the initiation of blooms, following ash input (Hamme et al., 2010; Achterberg et al., 2013). These findings are supported by both remote sensing observations (e.g., Langmann et al., 2010; Kelly et al., 2023) and laboratory-based incubation experiments (e.g., Mélançon et al., 2014), despite the limited number of direct observations. However, significant gaps remain in our understanding of the effects of ash deposition on marine ecosystems. No single study uses all the available methods (e.g., direct observations and sample collection, incubation experiments, satellite observations, modelling) to assess the impact of volcanic soluble Fe on phytoplankton blooms. Key uncertainties include:

1) How ash deposition fluxes and composition affect the duration and scale of blooms;
2) Whether very large eruptions could cause significant CO_2 drawdown from the atmosphere;
3) What the fractional Fe solubilities of different compositions of ash are;
4) Whether the acidity of the volcanic plume could enhance Fe solubility of ash;
5) Which elements and elemental ratios might have beneficial or adverse effects on different phytoplankton species;
6) Whether the same ash composition can impact different species in different ways.

More direct observations would help address these uncertainties, but such events are unpredictable and logistically difficult to study in real time. As a result, there is growing interest in developing proxy methods to reconstruct phytoplankton responses to past eruptions, for example, by

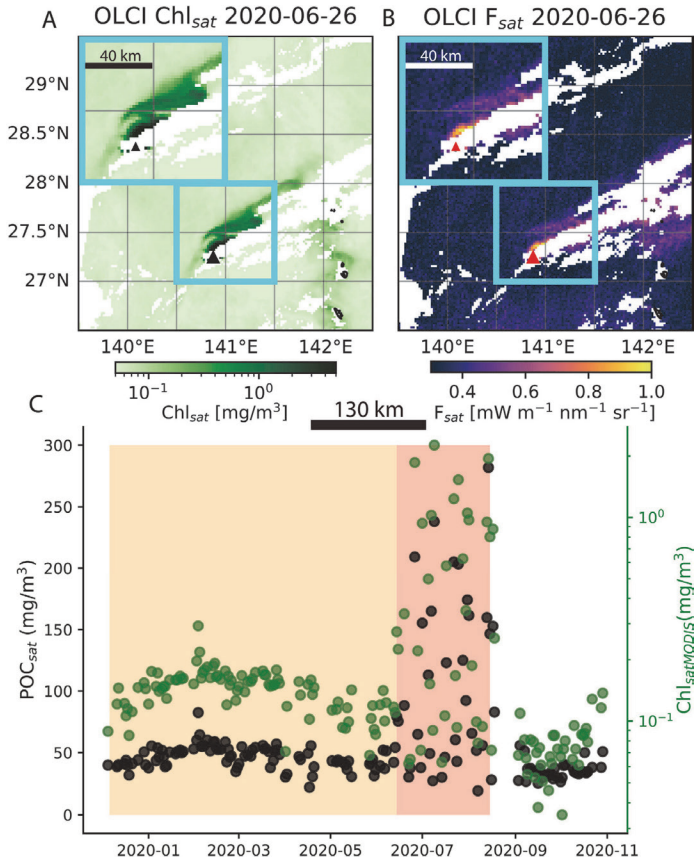

Fig. 5. Satellite data measured via the Ocean and Land Color Instrument (OLCI) onboard Sentinel-3 A/B from the 2020 Nishinoshima eruption, Japan showing (a) chlorophyll-*a* imagery, (b) fluorescence imagery, and (c) timeseries data with the red box highlighting the explosive eruption horizon relative to $Chl_{SatMODIS}$ (chlorophyll-*a*) and POC_{Sat} (particulate organic carbon) measurements. Figure reprinted from Kelly et al. (2023) with permission: https://creativecommons.org/licenses/by/4.0/.

analysing ash layers, trace elements, and organic proxies of phytoplankton preserved together in high-temporal resolution ice cores.

It should be noted that linking satellite observations to eruptive deposits without field observations is complex and may not always provide a definitive conclusion (e.g., Barone et al., 2022; Whiteside et al., 2023). With ocean colour satellite data, spatial coverage is important and can be incomplete for very short periods such as sporadic eruptions. For similar reasons, spatial coverage may also hide long term trends, introducing uncertainty in background conditions (Browning et al., 2015).

4–5 Indirect impacts of ash on primary productivity

Large scale explosive eruptions can inject huge quantities of volcanic ash and aerosols into the stratosphere, which reflect solar radiation and can contribute to global cooling and a reduction in sunlight reaching Earth's surface in the following years (Rampino & Self, 1984; Robock, 2000), with potentially severe implications for primary productivity. There are many well-documented examples of historic eruptions which have resulting in such cooling, including Samalas 1257 (up to 1°C; Guillet et al. (2017); Wade et al. (2020)), Tambora 1815 (0.4−0.8°C; Stothers (1984)), Zavaritskii 1831 (~1°C NH; Hutchison et al. (2024)), and Pinatubo 1991 (~0.5°C; McCormick et al. (1995); Parker et al. (1996)). Significant changes in global temperature and sunlight availability as a result of volcanic activity may have implications for marine phytoplankton productivity over proceeding years, although there are no existing studies which have investigated this topic. Volcanic induced cooling may also decrease SSTs, which could affect ocean stratification and mixing, altering phytoplankton productivity. Non-volcanic studies of

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periodically decreased temperatures have noted mixed effects on phytoplankton, as cooling can enhance vertical mixing in the water column, leading to increased phytoplankton biomass (e.g., Fernández-González et al., 2022; Theodorou et al., 2025). However, this effect seems to vary spatially, with nutrient content in the water being more important for blooms than temperature changes.

Decreases in sunlight caused by increased aerosol optical depth (AOD) from volcanic ash plumes may also limit phytoplankton productivity even when nutrients are available, especially in light-limited high latitude regions. Qu et al. (2014) examined satellite-derived chlorophyll-*a* concentrations in the Greenland Sea along with AOD, and observed a correlation between the two parameters, suggesting that higher AOD may act to decrease phytoplankton populations.

There are many limitations in understanding indirect volcanic effects on marine phytoplankton productivity, as to date no studies have directly investigated the influence of volcanic-induced cooling and reduced sunlight on phytoplankton dynamics over subsequent years. This may be because these effects would only be derived from larger scale, less frequently occurring eruptions. Additionally, the complex interactions between volcanic aerosols, SST, ocean stratification, and nutrient availability make it challenging to isolate volcanic effects from other environmental factors.

5. Impacts of very large eruptions and future research directions

Most of the examples in **Section 4** have focussed on volcanic ash delivered to the ocean by relatively small, historic eruptions. However, the greatest potential for widespread impacts comes from large, explosive eruptions including caldera-forming events, which can spread vast amounts of ash across global oceans, regardless of the source location (Fig. 3). As there have been no such events during modern instrumental times, the impacts that the largest magnitude volcanic events may have on ocean biogeochemical cycles remains unknown. It can be hypothesised that larger events producing voluminous quantities of ash (up to those including supereruptions ejecting >1000 km^3 ash) may have had significant and potentially ongoing impacts on primary productivity, with carbon drawdown from the atmosphere in the years to decades following an eruption (Self & Blake, 2008).

Marine sediment cores containing widespread ash layers contain important paleoenvironmental information in sediment chemistry and foraminifera chemistry, which can be used to infer changes in marine and climate conditions (e.g., Waelbroeck et al., 2019; Hathorne et al., 2023). Such archives could be used to infer post-eruption impacts on the ocean. However, low sedimentation rates in the deep ocean means that changes are interpreted over centuries or millennia: timescales that are too coarse to interpret marine productivity changes in the months to years following eruptions (e.g., Wilkinson, 2024).

One archive which we anticipate could be useful to look further into the geological record for evidence of primary production changes in response to large-scale explosive volcanic events, is polar ice cores. Ice cores preserve a range of chemical proxies including those for past volcanism (e.g., Sigl et al., 2015; Abbott et al., 2024), palaeoclimatic (e.g., Mayewski et al., 2017; Kravchinsky et al., 2025) and marine biogeochemical change (Thomas & Abram, 2016; King et al., 2019; Winton et al., 2022; Wauthy et al., 2024) at high temporal resolution (typically months to years). Certain proxies can be sampled to determine deposition fluxes of bioavailable Fe which are critical for interpreting phytoplankton productivity in the past. While no existing work has focused specifically on ash-derived Fe sources for this purpose, the contribution of aeolian dust and biomass burning to Fe fertilisation has been studied in Antarctica (e.g., Edwards & Sedwick, 2001; Winton et al., 2014; Winton et al., 2016) and represents a suitable analogue for the methodology. For example, Winton et al. (2016) evaluated the fractional Fe solubility in a snow pit from Roosevelt Island, in the eastern Ross Sea, and estimated that the dFe and TDFe (total dissolvable iron) fluxes at this site from 2011/2012 were high, and the observed background fractional Fe solubility of ~ 0.7 % was found to be consistent with a mineral dust source (Winton et al., 2016). Applying this method to estimate the flux of instantaneously soluble Fe derived from ashfall from an explosive event could provide insights into the fertilising potential of erupted ash on primary production.

The use of phytoplankton-sourced organic proxies in ice cores could also provide insights into phytoplankton productivity and composition through time, including changes over the course of an ash deposition event (Rhodes et al., 2009; King et al., 2019; Fogwill et al., 2020). There are three different phytoplankton proxies currently employed in ice cores. Methanesulfonic acid (MSA; CH_3SO_3H) is widely used as a proxy for marine primary production and sea ice extent, and has also been linked to localised phytoplankton blooms

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following volcanic ash deposition (e.g., Polashenski et al., 2018). Fatty acid lipid biomarkers (e.g., oleic acid) are indicators of microalgae and allow class-specific chemotaxonomic identification of phytoplankton (Sahu et al., 2013; King et al., 2019; de Jong, 2024; Pokhrel et al., 2025). Fluorescent dissolved organic matter (fDOM) is another method used to characterise organic matter in ice cores, as fDOM sources can be distinguished by excitation-emission wavelengths (Fogwill et al., 2020; Jung et al., 2020; D'Andrilli & McConnell, 2021). If a large, explosive eruption resulted in extensive phytoplankton blooms, changes in the composition and/or abundance of biomarkers across the eruption horizon might be expected. In conjunction with MSA and bioavailable trace metal concentrations from ice cores, these records could greatly enhance our understanding of eruption-driven phytoplankton responses from past eruptions. There are a number of limitations with these experimental approaches, including the fact it would only work to robustly constrain the impacts of a small number of eruptions which can be geochemically identified via the presence of glass shards in polar ice cores (e.g., Dunbar et al., 2017).

6. Conclusions

Volcanic ash deposition plays a significant role in regulating ocean biogeochemical cycles, particularly by directly influencing phytoplankton blooms. This review highlights that volcanic eruptions deliver key bioavailable trace metals to the surface ocean, which can stimulate phytoplankton growth in regions where productivity is otherwise limited by natural ocean conditions. Chemical processing within the acidic plume can also enhance the Fe solubility of ash, resulting in greater biological impacts. Direct observations, such as following the 2008 Kasatochi and 2010 Eyjafjallajökull eruptions, demonstrate the potential of ash-driven Fe fertilisation to trigger phytoplankton blooms, with measurable impacts on carbon dioxide drawdown. Such observations are scarce and largely opportunistic, but laboratory-based experiments and satellite observations support these findings. However, significant uncertainties remain regarding the broader impacts of eruptive deposits on phytoplankton communities. For example, differing metal ratios from volcanic ash may promote the growth of some species, while inhibiting others. Additionally, large-scale eruptions in the geological past may have driven more substantial phytoplankton responses across wide regions, potentially contributing to enhanced carbon sequestration and therefore contributing indirectly to volcanic cooling. Better understanding of how phytoplankton populations respond to ash input and the associated flux of micronutrients is vital, as these organisms form the foundation of marine ecosystems and play a crucial role in regulating climate and nutrient cycling. We suggest that future research should prioritise better understanding the range of ecological and climatic consequences of volcanic ash deposition in the oceans, particularly for the highest magnitude volcanic events.

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