

## Volcanic and atmospheric controls on ash iron solubility: A review

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### ABSTRACT

The ash material produced by volcanic eruptions carries important information about the underground magma eruptive conditions and subsequent modifications in the volcanic plume and during atmospheric transport. Volcanic ash is also studied because of its impacts on the environment and human health. In particular, there is a growing interest from a multidisciplinary scientific community to understand the role that ash deposition over open ocean regions may play as a source of bioavailable Fe for phytoplankton production. Similar to aeolian mineral dust, the processes that affect the mineralogy and speciation of Fe in ash may promote solubilisation of Fe in ash, and thus may increase the amount of volcanic Fe supplied to ocean surface waters. Our knowledge of these controls is still very limited, a situation which has hindered quantitative interpretation of experimental Fe release measurements. In this review, we identify the key volcanic and atmospheric controls that are likely to modulate ash Fe solubility. We also briefly discuss existing data on Fe release from ash and make some recommendations for future studies in this area.

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### 1. Introduction

Volcanic ash is the fine-grained tephra material produced during an eruption and which has particle diameter ( $p_d$ ) ranging from submicron to less than two millimetres (Heiken, 1972; Horwell, 2007). A substantial mass of ash is injected into the atmosphere yearly; for example, the average emission of fine ash ( $p_d < 63 \mu\text{m}$ ) is estimated to be  $\sim 176\text{--}256 \text{ Tg yr}^{-1}$  (Durant et al., 2010). Whilst this input is relatively small compared to the terrigenous dust load ( $1000\text{--}3000 \text{ Tg yr}^{-1}$ , Tegen and Schepanski, 2009), single large eruptions may have a sizeable but temporary effect on the particle loading of the atmosphere (Mather et al., 2003). Ash produced by strong explosive events can be transported several thousands of kilometres away from the volcanic source. Across the globe, and particularly for the several hundred volcanoes located along the Pacific Ring of Fire, a substantial fraction of the ash erupted can be deposited over the open ocean. For example, during the 1991 eruption of Mt. Pinatubo volcano in the Philippines, at least  $3000 \text{ Tg}$  of ash fell over the South China Sea (Wiesener et al., 1995), whilst the 2008 eruption of Kasatochi volcano, Alaska, deposited  $\sim 370 \text{ Tg}$  of ash over a  $77.6 \times 10^5 \text{ km}^2$  area of the subarctic North Pacific (Langmann et al., 2010a). Furthermore, the marine sediment records are punctuated by ash layers, ranging from millimetres to metres in thickness (Cather et al., 2009; Straub and Schmincke, 1998), evidencing the frequency of such deposition events throughout the geologic past.

The growing scientific interest for understanding the impact of ash deposition on the ocean (see review by Duggen et al., 2010) stems from the well-documented work on the iron (Fe) input to many open ocean regions by aeolian mineral dust sourced in arid or semi-arid regions. Iron is a micronutrient which plays an important role in regulating phytoplankton growth in the ocean (Boyd et al., 2000; Coale et al., 1996; Kustka et al., 2003; Martin et al., 1994, 1991) and it also can (co)-limit marine nitrogen fixer organisms in oligotrophic areas (Mills et al., 2004). Mineral dust is recognized as the primary source of Fe to the remote open ocean (Duce and Tindale, 1991; Jickells et al., 2005). Similar to mineral dust, ash Fe solubility (i.e., the water-soluble mass fraction of Fe in ash, in%) is a key parameter for assessing the potential of ash deposition to modify the surface ocean Fe budget. Duggen et al. (2010) report that the experimentally-measured Fe release from ash produced by subduction zone and hot spot volcanism is in the ranges  $100\text{--}400$  and  $35\text{--}107 \text{ nmol Fe g}^{-1}$  ash, respectively. Assuming a typical total Fe content in ash of  $2\text{--}8 \text{ wt.}\%$  (see Section 2.1), these values indicate an Fe solubility of  $<0.01\text{--}0.1\%$ , but some ash specimens can display higher values (up to  $\sim 1\%$ ). In comparison, the typical solubility of Fe in mineral dust is at least one order of magnitude higher ( $1\text{--}2\%$ , Jickells and Spokes, 2001), despite a lower total Fe content ( $3 \text{ wt.}\%$  on average, Jickells et al., 2005).

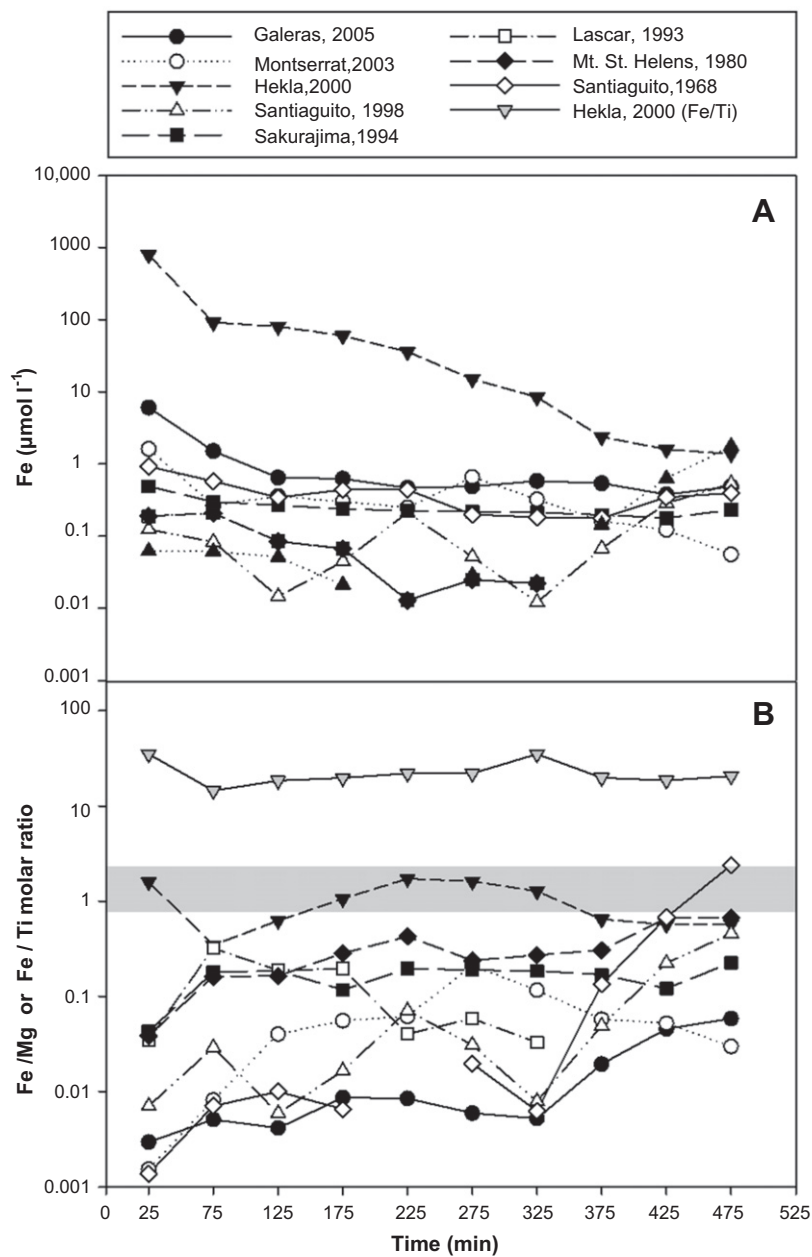
Although Fe solubility in ash is relatively low, there is mounting evidence that ash deposition has the potential to alter the Fe budget in the surface ocean (Hamme et al., 2010; Langmann et al., 2010b; Lin et al., 2011). The most convincing data were collected following the August 2008 eruption of Kasatochi volcano in Alaska. Both satellite images and detailed in situ sampling recorded one of

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the largest phytoplankton blooms observed in the subarctic North Pacific (Hamme et al., 2010; Langmann et al., 2010b). The field observations confirmed previous experimental measurements, which showed that upon contact with sea and de-ionised water, ash can release Fe in quantities sufficient to instigate a positive response of oceanic phytoplankton, particularly in Fe-limited ocean regions (Duggen et al., 2007). These results have revived the idea that large-scale volcanic explosive events in the past instigated climate changes through ash-mediated disruptions of the ocean carbon cycle (Bay et al., 2004; Cather et al., 2009; Jicha et al., 2009).

According to recent dissolution experiments, the pattern of Fe release from ash exposed to (sea)water is characterized by transient high initial values followed by lower and more or less steady values (Fig. 1a; Duggen et al., 2007; Frogner et al., 2001; Jones and Gislason, 2008). Jones and Gislason (2008) indicated

that the majority of Fe was liberated in the first hour, typically 40–90% of the total released in 8 h. The presence in ash of at least two pools of Fe with distinct solubility is usually held responsible for this behaviour. Thus, the amount of volcanic Fe susceptible to be released from the ash upon contact with water is not simply controlled by total Fe content. In fact, the few measurements available indicate that Fe solubility does not correlate with bulk Fe in ash (Jones and Gislason, 2008; Olgun et al., submitted for publication). By analogy with mineral dust, ash Fe mineralogy and speciation must be considered when attempting to predict the rate and extent of Fe dissolution in all aqueous environments. However, various volcanic and atmospheric controls may affect these properties in the ash. Currently, understanding of ash Fe solubility and its controls is hindered by a lack of data, a problem already alluded to in Duggen et al.



**Fig. 1.** Fe concentrations in solution from the leaching of selected volcanic ash samples under a sustained  $60 \pm 5 \text{ ml h}^{-1}$  flow of deionised water (A), and temporal variation in Fe/Mg and Fe/Ti ratios in solution (B), compared to Fe/Mg and Fe/Ti ratios determined in bulk chemical analysis of the ash, indicated by the grey box. Data from Jones and Gislason (2008).

(2010)'s detailed review on the role of airborne ash for the surface ocean biogeochemical Fe cycle.

Our objective in this paper is to provide new insights into the volcanic and atmospheric controls that may modulate ash Fe solubility. We review the state of current knowledge concerning the content, mineralogy and speciation of Fe in volcanic ash and we emphasize the importance of the ash surface for Fe solubility. We then discuss the potential impact of volcanic and atmospheric processing on ash Fe mineralogy and speciation. A brief evaluation of the existing experimental measurements of Fe release from ash is also provided before concluding the paper with some recommendations for future work.

## 2. Iron in volcanic ash

### 2.1. Iron in the ash bulk

In large volcanic explosive eruptions, the fundamental process driving ash generation is the mechanical fragmentation of magma (i.e., the process through which a bubbly or foamy magma is transformed into a gas–solid fragment dispersion) within the subsurface volcanic conduit (Dingwell, 1996). Ash is typically composed of silicate glass and crystalline materials inherited from the magma itself, but also from the conduit rocks eroded during the eruption (Heiken and Wohletz, 1992). Iron in ash occurs in different forms, including as a component of the glass and as primary Fe-bearing silicate and Fe-oxide minerals. Non-magmatic Fe-bearing phases, such as clay, sulphide and sulphate minerals, formed through hydrothermal alteration can also be entrained in the ash particles. However, for large explosive events, this particular mineralogy corresponds typically to the initial eruption stage, and overall represents a minor contribution to the total Fe emitted in ash (Heiken and Wohletz, 1992) and therefore, it will not be discussed further. Since the components of ash occur in different proportions depending on magma and eruption style, the total content, mineralogy and speciation of Fe vary accordingly.

The total Fe content in ash primarily reflects that of the magma from which it derives. Magmas encompass a broad range of compositions, but in general Fe content increases with decreasing Si content, from less than 2 wt.% in a typical rhyolite to 7–8 wt.% in a typical basalt composition (Le Maitre, 1976; Rogers and Hawkesworth, 2000). This variation is either the result of partial melting of mantle or crustal rocks with different compositions, or the product of differentiation of a single parent magma (Rogers and Hawkesworth, 2000). The oxidation state of magma dictates the speciation of Fe within it. Le Maitre (1976) made a detailed studies of magmatic rocks and found that the mean ferrous iron to ferrous and ferric iron ratios (wt.% FeO/(FeO + Fe<sub>2</sub>O<sub>3</sub>)) of the common igneous rocks ranged from 0.38 to 0.77, the basalt rocks being less oxidised than those high in silica. However, the oxidation ratio measured in freshly-deposited ash may not necessarily reflect that of the source magma due to oxidation processes occurring within the eruption plume (see Section 3.1; Horwell et al., 2003; Moriizumi et al., 2009).

Within the glass, ferric iron (Fe<sup>3+</sup>) is commonly found in substitution for Si<sup>4+</sup> in the silicate network, providing a neighbouring monovalent or divalent cation is available to compensate the charge deficit generated (Mysen and Richet, 2005). On the other hand, ferrous iron (Fe<sup>2+</sup>) can occupy the interstices between the silicate tetrahedra, alongside other divalent cations such as Ca<sup>2+</sup> and Mg<sup>2+</sup> (Mysen and Richet, 2005). The distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup> within the glass is a complex function of its composition and oxidation state (Mysen and Richet, 2005), the latter being governed by magma conditions (pressure, temperature, volatile saturation) at the time of formation and ascent towards the surface.

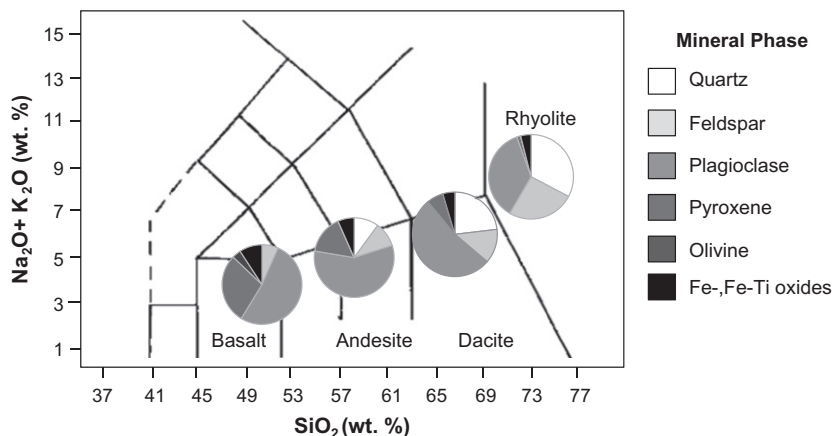
Various Fe-bearing crystalline phases, including aluminosilicates and oxides, whose formation can be traced to the source magma, may occur within the ash glassy component and/or as individual crystals in the ash material. In aluminosilicates, Fe (in both redox states) is essentially found in various proportions in the ferromagnesian minerals olivine, pyroxene, amphibole and biotite (Bladh and Speer, 2001). In addition, Fe may be associated with feldspars, when Fe<sup>2+</sup> substitutes Ca<sup>2+</sup> (Smith, 1974a, 1974b). Non-silicates Fe-bearing phases may also be present within the ash, including iron oxides and iron sulphide species. Iron oxide minerals in ash consist mainly of magnetite (Fe<sub>3</sub>O<sub>4</sub>), titanomagnetite (Fe<sub>2</sub>TiO<sub>4</sub>) and ilmenite (FeTiO<sub>3</sub>). As illustrated in Fig. 2, the proportions of ferromagnesian and Fe-oxides in ash decrease with increasing total silica content. The Fe-oxides are the less abundant Fe-bearing phases across selected basaltic, andesite, dacite and rhyolite compositions as they usually comprise less than 10% of the total crystal content. Iron sulphide (pyrrhotite, Fe<sub>(1-x)</sub>S, where *x* is a stoichiometric coefficient) can be stable in reducing magmas (Scaillet et al., 1998; Webster and Botcharnikov, in press). Other phases, commonly encountered in mineral dust from arid regions, such as hematite (Fe<sub>2</sub>O<sub>3</sub>), Fe oxyhydroxides (e.g., goethite, ferrihydrite) and Fe-containing clays (e.g., Fe-smectites) are absent from freshly-erupted ash formed through magma fragmentation. However, these phases may form during volcanic and/or atmospheric processing, a point discussed later.

The broad compositional, mineralogical and speciation range displayed by volcanic ash at the point of emission already implies a complex pattern of Fe solubility. For example, it is known that Fe-oxides are less soluble in water than the Fe-bearing silicates (Journet et al., 2008; Stumm and Furrer, 1987). Further, the solubility of Fe in the latter group is influenced by its structural position (Brantley and Chen, 1995). Thus, a precise knowledge of the ash mineralogy is paramount to the description of the ash Fe solubility. It is also crucial for predicting the effect of secondary volcanic and atmospheric processes on Fe in ash (see Section 4).

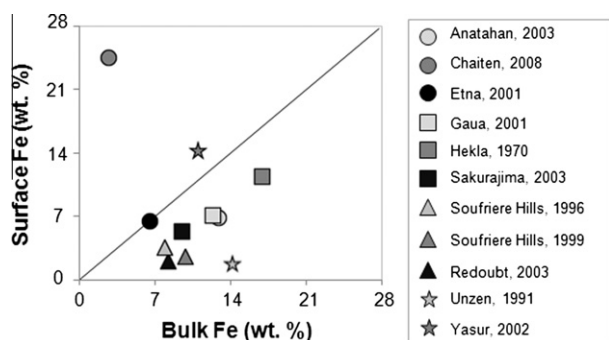
### 2.2. Iron in the ash surface

The surface Fe concentration measurements presented in Fig. 3 were obtained for 11 ash samples by using X-ray Photoelectron Spectroscopy (XPS), a technique which measures the elemental chemistry (composition and speciation) of the uppermost 2- to 10-nm-thick surface layer of a solid. For bulk compositions ranging from basalt to dacite, the data indicate that Fe is depleted in the surface of all but three ash samples (Yasur, Mt. Etna and Chaitén). Calcium and to a certain extent Mg were inferred to exhibit a similar pattern (Delmelle et al., 2007). The trend for volcanic ash samples contrasts with the reasonable agreement between the surface composition and bulk composition observed for mineral dust source materials (Cwiertny et al., 2008). This probably indicates that the surface of ash is subject to processes that can cause its composition to differ from that of the particle bulk. For example, Delmelle et al. (2007) tentatively explained Fe-depletion in the ash surface as being due to acid leaching of the particle surface during interaction with the volcanic gas/aerosol phase. However, such mechanism does not satisfactorily explain the Fe enrichment noted in Yasur and Chaitén ash, nor the agreement between bulk and surface Fe contents noted for Mt. Etna ash (see Section 5).

Whilst in-plume processing of the ash is likely to impact on the ash surface chemical properties (see Section 3), the mode of generation of the ash surface itself may also result in a surface which is different from the original bulk material. The surfaces of the erupted ash particles represent a mixture of pre-, syn- and post-eruptive surfaces. Pre-eruptive surfaces in the magma correspond to the boundaries between the silicate melt and the gas bubbles formed during exsolution of magmatic volatiles (Sparks, 1978) as well as to surfaces



**Fig. 2.** The relative abundance of specific mineral phases in rocks with basaltic, andesite, dacite and rhyolite compositions. Pie-chart centrepoints indicate  $\text{SiO}_2$  and total-alkali concentrations for each composition. Data from KWare Magma software (Wohletz, 1999).



**Fig. 3.** XPS surface to XRF bulk Fe ratios, from surface and bulk compositions (wt.%) normalised to 100% excluding O and C. Ash samples recovered from eruptions at Anatahan, 2003; Chaiten, 2008; Etna, 2001; Gaua, 2001; Hekla, 1970; Sakurajima, 2003; Soufriere Hills, 1996 and 1999; Redoubt, 2003; Unzen, 1991; Yasur, 2002.

exposed by a permeable network of fractures (Gonnermann and Manga, 2003 and references therein). Once created, such surfaces may undergo structural rearrangement in order to equilibrate with the surrounding physico-chemical conditions. This equilibration can proceed via various mechanisms; for example via the recombining of partially coordinated cations and anions to form new bonds; ionic diffusion processes; crystallisation; and phase separation or interaction with reactive gases (Dunken, 1982; Scholze, 1990), which in turn may affect Fe in the surface. Syn-eruptive surfaces represent new surfaces which form when eruptive fragmentation of the magma occurs in the brittle (solid-like) regime. It is well recognised that silicate glasses of different compositions show various resistances to both compressive and tensile stresses (Scholze, 1990). Therefore, the multi-component volcanic glass probably features regions within its silicate network which are more prone to fracturing than others. This may be particularly the case where crystallisation has occurred. Industrial glass studies reveal that the formation of crystalline phases promotes the formation of fractures within the surrounding glass (Scholze, 1990). Since crystallisation derives its cations and anions from the bulk material, fracturing may expose surfaces depleted in the chemical elements incorporated into the crystal phases. Thus, crystallisation of Fe-bearing minerals in the magma may result in a reduced Fe content in the syn-eruptive surfaces associated with fractures.

Communication by collision between ash particles or between ash particles and conduit wall rock after magma fragmentation may also form new ash surfaces (post-eruptive), which may exhibit compositional and mineralogical differences when compared to

the bulk ash material. This secondary mode of ash generation may become significant in the case of large-scale eruptions, which produced extensive co-ignimbrite ash clouds (Darteville et al., 2002; Sparks et al., 1997). In such cases, the ash material tends to be finer and therefore, has a longer residence time in the atmosphere and a higher chance of being deposited over oceanic areas.

Since Fe release from ash exposed to water is an interfacial (ash/liquid) process, the Fe content, mineralogy and speciation in the ash surface is central to the description of the ash Fe solubility. However, there is a patent lack of data and more work is needed in order to fully appreciate the factors which govern the presence of Fe in the surface of ash before further processing of the material in the eruption plume and the atmosphere.

### 3. Volcanic processing of ash

#### 3.1. High-temperature chemical reactions

Iron oxidation in silicate glass has been shown to proceed via different mechanisms (Cook and Cooper, 2000; Cooper et al., 1996; Mysen and Richet, 2005 and others). Studies on hydrous rhyolite and anhydrous basaltic compositions reveal that the inward propagating oxidation of  $\text{Fe}^{2+}$  which begins at the glass surface is diffusion-controlled (Cooper et al., 1996; Moriizumi et al., 2009). The key result of oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is the restructuring of the glass silicate network to allow  $\text{Fe}^{3+}$  to exist in tetrahedral coordination, providing that alkali cations are able to compensate the negative charge created. However, where alkali cations are not available, formation of discrete  $\text{Fe}^{3+}$  bearing phases occurs (Cooper et al., 1996). These phases may include ferric oxides (Ayris, 2010), titanomagnetite (Burkhard, 2001) and more complex multi-component phases such as  $\text{Fe}^{3+}$ -bearing spinels (Cook et al., 1990) and pyroxenes (Ayris, 2010; Burkhard, 2001). In the same way, the  $\text{Fe}^{3+}$  produced by oxidation of  $\text{Fe}^{2+}$  in ferromagnesian minerals may remain as structural  $\text{Fe}^{3+}$  cations, or become segregated into discrete  $\text{Fe}^{3+}$ -bearing phases, such as hematite (Straub et al., 1991). At high temperature (>550 °C), bulk oxidation of magnetite also can form hematite; whilst at lower temperatures (200–375 °C), the reaction is limited to the surface (Lepp, 1957).

In air-only atmospheres, the presence of  $\text{O}_2$  was posited to initiate glass surface oxidation (Burkhard, 2001; Cook and Cooper, 2000; Cooper et al., 1996). However, although initiated by gas-surface interaction, the inward propagation of the Fe oxidation front is driven by a structural rearrangement coupled with an outward divalent cation diffusion (Cooper et al., 1996). A similar

mechanism could act in the presence of magmatic O<sub>2</sub>-bearing gases such as H<sub>2</sub>O and SO<sub>2</sub>, which are entrained in the rapidly ascending hot gas-ash mixture released through magma fragmentation. Previous authors have determined that at 800 °C in both basaltic glass and rhyolite tephra, the diffusion-controlled Fe oxidation mechanism can be described by diffusion coefficients of 10<sup>-15</sup>–10<sup>-16</sup> m<sup>2</sup> s<sup>-1</sup> (Cooper et al., 1996; Moriizumi et al., 2009). Using Fick's second law of diffusion (Mehler, 2007), and an ascent time through the volcanic conduit for a gas-ash dispersion generated by a dacitic explosive eruption of 40 s (Mastin, 2002), it can be calculated that an Fe oxidation front could propagate up to 60–200 nm into particle surfaces prior to subaerial emission. This result is noteworthy and suggests that oxidation reactions of the ash glassy component at high temperature can have a determining impact on the mineralogy and speciation of Fe in the ash surface. This is of significance when considering further chemical reactions involving Fe as the ash is subjected to volcanic and atmospheric processing (see Sections 3.2 and 4.2). Moreover, oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> in the ash may represent a decrease in Fe bioavailability as Fe<sup>3+</sup> is thought to be less accessible to marine phytoplankton (Cwiertny et al., 2008).

Along with ash, magma fragmentation also releases volatile species. The major gases are H<sub>2</sub>O vapour and CO<sub>2</sub> which together account for >90 mol.%. Sulphur dioxide, H<sub>2</sub>S, HCl and HF also occur but in lower concentrations (typically <2–3 mol.%). In addition, various metal cations can be released from the hot magma, but Fe is not one of them because it is usually present only in trace amounts due to its low volatility at magmatic temperatures (Symonds et al., 1987). It has long been known that gas-ash interaction in the eruption plume leads to volatile scavenging, in particular SO<sub>2</sub>, HCl and HF (Rose, 1977; Óskarsson, 1980). The reactions between these gases and the ash surface are thought to be partly responsible for the deposition of alkali and alkaline-earth sulphate and chloride salts at the ash surface. Several authors (Frogner et al., 2001; Duggen et al., 2007) have assumed that such reactions also form Fe-bearing salts in the ash surface. However, Fe-bearing salts on ash particle surfaces produced in explosive eruptions, or in ash and glass materials exposed to SO<sub>2</sub>, HCl or HF in laboratory experiments has yet to be confirmed (Óskarsson, 1980; P. Ayris et al., unpublished data, 2010).

Based on experimental results (Óskarsson, 1980; P. Ayris et al., unpublished data, 2010), it is likely that Fe as a component of the glass network or within discrete crystalline phases in the ash does not participate to a significant extent to the scavenging of SO<sub>2</sub>, HCl and HF. However, the possibility of H<sub>2</sub>S reaction with Fe in the ash has not been previously considered. Depending on the redox state of the source magma and its evolution during ascent and degassing, H<sub>2</sub>S can be present along with SO<sub>2</sub> in the gaseous eruptive phase (Burgisser and Scaillet, 2007). Iron oxides, including hematite and magnetite within coal ash (Schrodt et al., 1982), are known to be efficient sorbents for the removal of H<sub>2</sub>S from industrial flue gas streams at temperatures of up to 700 °C, with less efficient H<sub>2</sub>S scavenging at higher temperatures being possible (Ren et al., 2010; Slimane and Abbasian, 2001; Yumura and Furimsky, 1985). The product of these reactions is an insoluble Fe sulphide phase. As volcanic ash contains magnetite, the same desulphidation reaction may be expected to occur. Further reaction with SO<sub>2</sub> at temperatures above ~500 °C may convert the Fe sulphide into an Fe sulphate (FeSO<sub>4</sub>) phase (Mellor, 1935), whilst at lower temperatures (~290–430 °C), partial oxidation of Fe sulphide may result in the formation of magnetite and an unstable sub-sulphide (Fe<sub>2</sub>S<sub>3</sub>) phase (Galwey, 1997).

### 3.2. Low-temperature chemical reactions

At lower temperatures in the eruption plume, additional heterogeneous reactions involving a liquid phase and the ash material

take place. In the eruptive gas phase, some of the SO<sub>2</sub> oxidises to sulphite (SO<sub>3</sub>), which upon cooling of the effluent readily reacts with water vapour to form vapour-phase sulphuric acid (H<sub>2</sub>SO<sub>4(v)</sub>). As cooling continues, the ash particle temperature eventually drops below the dew point of the complex gas mixture, allowing condensation of the H<sub>2</sub>SO<sub>4(v)</sub> onto the ash surfaces, soon followed by water and the halide acids (HCl and HF). Sulphuric acid has the highest dew point of all these constituents and therefore, always condenses first (Verhoff and Banchemo, 1974). This process is expected to lead to high concentrations of dissolved H<sub>2</sub>SO<sub>4</sub> in the condensate associated with the ash, and thus to strongly acidic pH values. The presence of liquid acids on ash explains the pronounced pH depression (>3 pH units) observed for some ash samples when ash was exposed to near-neutral pH water (e.g. Hinkley and Smith, 1982; Jones and Gislason, 2008). Assuming that 1–10% of the ash particle mass is coated with aqueous acid (Delmelle et al., 2005; Schumacher, 1988) and knowing the ash-to-water ratio used in the leaching experiment, it is inferred that pH values less than one can develop in the aqueous film occurring on the ash surface.

The low pH conditions of the aqueous film undoubtedly promote acid leaching and dissolution of the Fe-bearing phases present in the ash material, with potentially important repercussions for the ash Fe solubility in seawater. In general, pH is believed to exert a primary control on aqueous Fe release from the ash's silicate components as silicate dissolution rate increases exponentially with decreasing pH (Gislason and Oelkers, 2003; Oelkers and Gislason, 2001). Whilst there is a paucity of data on Fe-oxide dissolution at low pH values, the same relationship probably applies (Arlaukas et al., 2004; White and Peterson, 1990). In the case of titanomagnetite, the stoichiometry of Fe cations release was shown to be modulated by pH; with Fe<sup>2+</sup> being liberated preferentially relative to Fe<sup>3+</sup> at pH values ≥3.8 (White and Peterson, 1990). Solution chemistry, other than pH, is also thought to affect silicate dissolution rate. For example, complexation of aqueous Al with anions such as sulphate and fluoride enhances glass dissolution rates significantly (Flaathen and Gislason, 2007; Gislason and Oelkers, 2003; Wolff-Boenisch et al., 2004).

The composition and mineralogy of ash are additional factors which are likely to influence the ash Fe solubility in acidic conditions. At pH 4, dissolution rates for both minerals and glasses decrease with increasing Si:O ratio, but glass dissolution rates are faster than corresponding mineral rates (Wolff-Boenisch et al., 2006). At lower pH, this may no longer be the case as Hamilton and Pantano (2000) indicate that the dissolution rates of albite crystal and glass measured at pH 2 are almost indistinguishable. The results of low-pH experiments (at 75 °C) suggest that plagioclase dissolves from crushed basalt faster than pyroxene (Hurowitz et al., 2005). In contrast, McAdam et al. (2008) predicted an opposite trend, in accordance with Rowe and Brantley (1993)'s and van Hinsberg et al. (2010)'s field observations for andesitic rocks leached by magmatic hydrothermal acidic fluids (pH ≤ 2). The coordination of Fe in the silicate mineral structure may affect its release rate; in pyroxenes and amphiboles, cations, including Fe<sup>2+</sup>, in the M2 (octahedral coordination) and M4 positions seem to be particularly prone to acid leaching (Brantley and Chen, 1995). Of note, site occupancies of Fe cations in the pyroxene crystal structure varies with the mineral composition (Bancroft et al., 1967), implying that the dissolution rate of Fe could diverge accordingly.

Journet et al. (2008) also reported a dependence of Fe solubility in plagioclase at pH 2 on the structural position of Fe, the highest value was inferred to correspond to Fe occurring as an interlayer ion. The same study concluded that the solubility of Fe in magnetite was lower than in two plagioclases (oligoclase and orthoclase). However, dissolution experiments performed on synthetic basalt and using a low pH (1.1) solution containing sulphate and chloride

revealed similar dissolution rates for titanomagnetite and a plagioclase (labradorite) (Hurowitz et al., 2005). These laboratory data further indicate a comparatively slower dissolution of the pyroxene phase (augite) present in the basaltic rock. Of note, Schott and Berner (1983) reported enhanced release of Fe relative to Si during dissolution of bronzite (pyroxene mineral) under oxic conditions at pH 1. Finally, as suggested earlier, oxidation of Fe in silicates and possibly Fe oxides due to gas-ash interaction at high temperatures in the plume could also affect Fe dissolution (e.g. Zhang, 1990).

Acid leaching and dissolution of the ash surface's mineral components following condensation of H<sub>2</sub>SO<sub>4</sub>, HCl and possibly HF in the cooling eruption plume probably creates etch pits at the surface of the silicate crystals (Berner et al., 1980; Schott and Berner, 1983). The development of etch pits in volcanic ash may increase surface area and is consistent with the hysteresis noted in N<sub>2</sub> adsorption-desorption isotherms carried out on various ash specimens (Delmelle et al., 2005). Interaction with HF in the eruption plume may be of particular importance as this may modify the reactivity of the ash surface, which will be later subjected to atmospheric processing. It may also affect the potential of the ash to release Fe upon contact with water. There is experimental evidence that pre-etching of feldspar and diopside with HF solutions changed the reactivity, perhaps by creating a fluoridated surface and by opening channels of transport that allow deeper penetration of hydrogen ions (Perry et al., 1983; Petit et al., 1987). The same effect might apply to the silicate components of ash.

The surface of the ash particles which have reacted with the acid condensates in the eruption plume can be coated with an aqueous film enriched in sulphate, chloride and sometime fluoride, as well as various cations, including Fe<sup>2+</sup> and Fe<sup>3+</sup>. The pH of this film will evolve depending on the initial acidity of the liquid, duration of contact time between the ash surface and the liquid, and acid buffering/neutralizing capacity of the ash material. If low pH values are maintained, Fe<sup>2+</sup> may remain present in solution due to sluggish oxidation kinetics under acidic conditions (Stumm and Lee, 1961). As the ash particles carried by the rising eruption plume reach the upper and drier atmosphere, evaporation of the low-pH, sulphate/chloride/fluoride-rich aqueous film emplaced at the ash surface is likely to take place. This process could eventually lead to saturation and formation of soluble Fe-sulphate/chloride/fluoride salts. Formation of both ferrous and ferric sulphate deposits following reaction of synthetic basalts with acidic (pH 0–1) sulphate/chloride-containing solutions and subsequent evaporation lends credence to this suggestion (Hurowitz et al., 2005; Tosca et al., 2004). Such salts are readily soluble and Fe associated with these phases can be rapidly leached upon contact with near-neutral pH water. After passage through the explosive eruption plume, the reacted ash (along with the modified eruptive gas/aerosol phase) begins its journey in the atmosphere as it is carried away from the volcanic source by the high-altitude winds. The cooled eruption plume which disperses in the atmosphere is commonly referred to as the volcanic cloud.

## 4. Ash processing in the atmosphere

### 4.1. Physical processing

Ash aggregates are often observed in ash deposits. The phenomena responsible for aggregation of ash particles is not fully understood, but is thought to be favoured at high humidities in the eruption plume and/or in the young volcanic cloud (Gilbert and Lane, 1994). Ash aggregation removes the fine particles from the gas-ash mixture, thus potentially altering the size spectrum of

the ash cloud advected in the atmosphere. In turn, this might affect Fe solubility if a relationship to particle size exists (see below).

Another physical mechanism that may modulate the potential for ash to release Fe in the open ocean is the preferential removal during long-range transport of larger and denser particles due to faster rates of gravitational settling (Folch et al., 2009). This phenomenon has been well documented through analysis of near-vent and distant ash deposits, where the proportions of fine-grained ash and silicate glass fragments increase away from the source (Varekamp et al., 1984). Some authors (Baker and Jickells, 2006; Ooki et al., 2009; Rubasinghege et al., 2010a) have suggested that the fractionation of mineral dust according to particle size exerts an important control on Fe solubility, possibly as a result of the increase of surface area-to-volume ratio in the finer particle population, but also due to the fact that small particles are enriched in clay minerals, which appear to have higher Fe solubility. However, the absence of clay phases in ash may limit the impact of physical processing on the ash Fe solubility to a size effect. Nevertheless, the glass enrichment in the distal ash material might enhance Fe solubility, since glass tends to dissolve faster than a crystalline phase with corresponding composition (Wolff-Boenisch et al., 2006).

### 4.2. Chemical processing

Laboratory studies on mineral dust suggest that several mechanisms can increase Fe solubility during atmospheric transport of mineral dust. For example, the presence of organic ligands (e.g., formate, acetate and oxalate) is thought to promote the photo-production of more soluble Fe<sup>2+</sup> (Baker and Croot, 2010 and references therein). Leaching and dissolution of dust following its mixing with, and uptake of acidic anthropogenic pollutants, including SO<sub>2</sub>, HCl and HNO<sub>3</sub>, is also regarded as a key pathway for enhancing dust Fe solubility e.g., (Meskhidze et al., 2003; Zhuang et al., 1992). Further, dust particles coated with sulphate and/or nitrate compounds can act as effective cloud condensation nuclei and thus, may undergo several cycles of condensation/evaporation in clouds. Cloud processing raises the relative concentration of the dissolved acids adsorbed onto dust and is also believed to have a strong impact on Fe solubility (Baker and Croot, 2010; Cwiertny et al., 2008; Desboeufs et al., 2001, 1999).

Ash in the atmosphere may endure processes similar to those mentioned above, but an important difference between ash and mineral dust is that the ash has already been exposed to acids in the eruption plume. As a result, further uptake of acids by the ash material may be limited due to the pH-dependent solubility of acid dissolution (Tolbert et al., 1988). However, this does not prevent the ash particles from nucleating cloud droplets, especially if acidic deliquescent compounds have formed on their surfaces (Textor et al., 2006). Thus, cloud processing is another mechanism through which ash Fe solubility may be further altered. For example, when the cloud droplets evaporate and the water is lost, Fe-sulphate/chloride salts may form due to saturation of the low-pH acidic film. During cloud processing, the ash material may also experience several cycles of large pH variations (acidic to near-neutral values; Pruppacher and Jaenicke, 1995; Wurzler et al., 2000). This may drive dissolution/precipitation reactions involving Fe as well as facilitate oxidation of dissolved Fe<sup>2+</sup> at higher pH values.

The extent to which atmospheric processing impact on the ash Fe solubility will not only depend on Fe mineralogy and speciation after passage of the ash through the eruption plume, but also on the capacity of the ash material to buffer acidity. Moreover, similar to observations made for mineral dust, the composition of the aqueous film coating the ash may play a role in dictating the extent of Fe dissolution at acidic pHs (Cwiertny et al., 2008; Rubasinghege et al., 2010b). Finally, it has been argued that the conditions of the last cloud evaporation/condensation cycle exert a larger influence

on mineral dust Fe solubility than the number of cycles (Desboeufs et al., 2001; Spokes et al., 1994). In the case of ash, this may imply that the residence time in the atmosphere is not a strong determinant of Fe solubility.

## 5. Measurements of iron release from volcanic ash

As mentioned earlier, a small number of studies have determined the release of Fe from ash in (sea)water (Duggen et al., 2007; Frogner et al., 2001; Jones and Gislason, 2008; Olgun et al., submitted for publication) but none of these have considered particle size and mineralogy and speciation of Fe. This is a serious limitation given that the ash materials used in these experiments had been exposed to various, but largely unconstrained, volcanic, environmental, storage and aging conditions. We have outlined in the preceding sections the predominant role of the ash surface in dictating ash Fe solubility. However, Fe release data are typically normalised to the ash sample mass (Frogner et al., 2001; Duggen et al., 2007; Jones and Gislason, 2008) and do not account for differences in surface area-to-volume ratio (as represented by the specific surface area,  $a_s$ ) associated with changes in particle size (and roughness). In general, the  $a_s$  of volcanic ash from explosive eruptions varies within a narrow window, i.e., <1 to a few  $\text{m}^2 \text{g}^{-1}$  (e.g. Delmelle et al., 2005; Horwell et al., 2003). Nevertheless, this variation could partly explain the range of Fe release/solubility values reported for ash. Thus, information on  $a_s$ , or at least on the particle size distribution, should accompany Fe release/solubility measurements carried out on ash samples from diverse origins.

The ash samples investigated so far (24 specimens in total) produced a roughly similar pattern of Fe release, i.e., high initial release followed by fast (within a few to <50 min) decline to lower and more or less steady values (Fig. 1a). In contrast, the second part of the release curve is thought to reflect comparatively sluggish dissolution of the ash's Fe-bearing silicates and oxide minerals. The presence of readily soluble Fe-bearing salts on the ash surface is usually evoked to explain the high initial liberation of Fe (Frogner et al., 2001; Duggen et al., 2007; Jones and Gislason, 2008), but whilst such salts remain unidentified on ash surfaces, other potential Fe sources should not be discounted. For example, generation of near-neutral pH values at the surface of the ash during cloud processing could lead to rapid precipitation of highly reactive

nanoparticles of ferrihydrite ( $\text{Fe}^{3+}$  oxyhydroxide) (Shi et al., 2009). Interestingly, Mackie et al. (2006) posited that the instantaneous soluble fraction of Fe in mineral dust may be represented by ferrihydrite. Clearly, careful mineralogical determinations are needed in order to partition the ash Fe into different solubility classes.

The ash erupted by Hekla volcano in 2000 was tested in two separate studies (Frogner et al., 2001; Jones and Gislason, 2008) and it consistently exhibited the highest Fe release in de-ionised water. The notable behaviour of the Hekla material could not be attributed to a particle size effect (Jones and Gislason, 2008). Instead, it may reflect a combination of strong acidity and elevated fluoride concentration in the eruption plume, which eventually promoted deposition of readily soluble Fe-bearing phases. However, such conditions may not be unique to this eruption, and additional processes may have contributed to the formation of soluble Fe. Petrological estimates indicate that the basaltic Hekla magma was held under reducing conditions prior to eruption and therefore, a significant fraction of the magmatic sulphur was probably degassed in the form of  $\text{H}_2\text{S}$  (Moune et al., 2007). We suggest that the origin of the soluble Fe in Hekla ash may also relate to efficient in-plume scavenging of  $\text{H}_2\text{S}$  by the ash's Fe-oxide constituents, according to reactions similar to those proposed in Section 3.2. The surface of the Hekla ash is Fe-depleted relative to the bulk (Fig. 3), but a lower surface Fe concentration in pre- and syn-eruptive surfaces which is then coated with Fe-bearing salts could still account for such a relationship. Fig. 1 was constructed based on Jones and Gislason (2008)'s experimental ash dissolution results and shows the evolution of the Fe concentration and Fe/Mg and Fe/Ti (Fe/Ti data available only for Hekla ash) molar ratios in solution as a function of time for eight ash samples. The Fe/Mg and Fe/Ti molar ratios in the bulk materials are also plotted. Except for Hekla, Fe/Mg was consistently lower at the beginning of the dissolution experiment in all the ash samples. The ratios then rapidly increased and varied significantly afterwards, but never returned to the initial values and remained below the Fe/Ti values in the bulk materials. This pattern suggests rapid dissolution at the ash surface of readily soluble phases containing significantly more Mg than Fe. Once this readily soluble pool was exhausted, Fe and Mg were released non-stoichiometrically from the ash's silicate and oxide components. The high initial Fe/Mg ratio value noticed for Hekla may point to an exceptionally large pool of highly soluble Fe; this

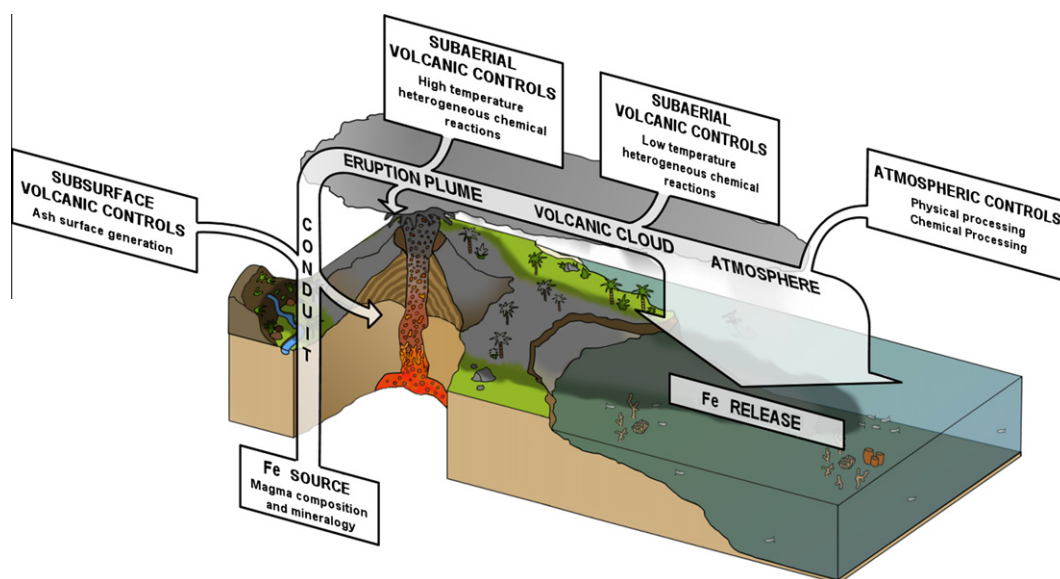


Fig. 4. Cartoon diagram showing the volcanic and atmospheric controls which dictate Fe solubility in volcanic ash.

is also supported by the shape of the Fe/Ti curve (Fig. 1b). The subsequent steady values of the Fe/Ti ratio suggest control by Fe/Ti-oxide dissolution. This may result from the low pH values (pH < 4.7) sustained throughout the ash dissolution experiments (Jones and Gislason, 2008).

## 6. Concluding remarks

Most explosive eruptions form fine volcanic ash, which through long-range transport in the atmosphere can add Fe to open ocean regions. There is growing evidence that ash may have an important complementary (albeit punctual) role to mineral dust in relieving the Fe-limitation in some parts of the oceans, thus potentially providing a link between volcanism and the global oceanic cycles of Fe and carbon. However, the factors that control the solubility of Fe in ash are very poorly understood and a thorough effort is needed before we can develop a quantitative appreciation of these controls. This is crucial for better assessing how large volcanic eruptions in the past may have affected the Earth's climate.

As illustrated in Fig. 4, our review shows that several volcanic and atmospheric factors govern overall ash Fe solubility. The source of Fe is the magma from which the ash originates and whose Fe content and mineralogy may vary on spatial and temporal scales. We distinguish the volcanic controls as being ash surface formation processes and high and low-temperature heterogeneous chemical reactions within the eruption plume. These controls are expected to have a marked influence on further (photo)chemical reactions during transport of the ash in the atmosphere. The measurement, interpretation and understanding of ash Fe solubility in relation to volcanic and atmospheric processing are in their infancy. However, there is a considerable body of literature dealing with Fe in mineral dust; the knowledge, methods and techniques used in these studies can easily be transferred to investigate the atmospheric controls on ash Fe. Inter-community discussion will certainly aid this progression.

We speculate that processing of the ash in the eruption plume is fundamental to the determination of the ash Fe solubility. A significant challenge lies in the establishment of experiments which can reproduce the range of physico-chemical conditions associated with volcanic eruptions. It is likely that this will be achieved through the use of model systems and through systematic measurements, including detailed mineralogical and chemical speciation analyses. Such approach is to be encouraged in order to formulate realistic conclusions regarding the volcanic processing of ash. Further, the fully characterised material generated in these experiments could be used in subsequent atmospheric processing studies. New insights may also be gained from careful examination of natural ash samples for which a well-documented volcanic and atmospheric "history" exists. Following Baker and Croot (2010)'s recommendations for investigating aerosol Fe solubility, the establishment of standard tools (reference materials and protocols) is essential if advance is to be made in understanding ash Fe solubility. Finally, the oceanic factors that ultimately determine the fraction and chemical speciation of ash Fe that is bioavailable have not been considered in this review but should clearly be integrated in future studies.

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