

Interactive comment on “Ash iron mobilization in volcanic eruption plumes” by G. Hoshyaripour et al.

G. Hoshyaripour et al.

gholamali.hoshyaripour@zmaw.de

Received and published: 29 May 2015

We thank the reviewer for the comments that helped us to improve this MS. The suggestions are applied in the revised MS. The questions and comments are answered below.

General Comments:

Comment 1: Notwithstanding the major problems identified below, it is also difficult to appreciate the study novelty. For example, it has long been known that oxidation and condensation of high-temperature volcanic gases produce hyper-acid sulfate aerosols in volcanic plumes. Uptake of halogen into such particles has been investigated theoretically by previous researchers (e.g., Martin et al. 2012). Similarly, the inverse rela-

C13256

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



tionship between silicate dissolution rate and pH at acid conditions is well-documented (e.g., Eick et al. (1996); Gislason and Oelkers (2003)). Enhanced dissolution rates also apply to iron oxides exposed to a low-pH aqueous solution (e.g., Hurowitz et al., 2006).

Reply: We agree with the reviewer that the mentioned theories are well known and documented in the literature. However, we should clarify three major points concerning the novelty of the current work.

First, a numerical model does not produce new concepts or laws that are not already included in the model. This is the fundamental essence of the model-based studies. In other words, numerical models are diagnostic tools to analyze the behavior of a system and/or to understand the observational data based on the known theories (Jacobson 2005, Seinfeld and Pandis 2006). Likewise, our study does not intend or claim to formulate any new law or concept concerning the volcanic gas and ash. Instead, it assimilates a wide range of well-documented mechanisms and processes from volcanology (e.g. Rose and Durant, 2009), eruption plume dynamics (e.g. Mastin 2007), Atmospheric chemistry (e.g. Jacobson 2005), ash dissolution (e.g. Oelkers and Gislason, 2001) etc. into a numerical model in order to quantitatively explain the ash-gas-aerosol interaction within the eruption plume. Therefore, similar to all model-based studies, the novelty of this work arises from investigating the role of “well-known” theories like those mentioned by the reviewer in governing the behavior of a “less-known” system here called “ash iron mobilization in volcanic eruption plumes”.

Second, the model presented in this study considers, for the first time, volcanic ash as a chemically active agent in the eruption plume. As it is mentioned in P. 32539 of the MS, previous modeling investigations on physical chemistry of volcanic eruption plumes have mainly focused on gas-phase chemistry (e.g., Bobrowski et al., 2007), micro-physical processes like condensation, scavenging and freezing (Tabazadeh and Turco, 1993; Textor et al., 2003) and also particle aggregation (Textor et al., 2006b, a) leaving the chemical interactions of the aqueous phase and the ash surface so far

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



nearly unexplored. Our study focuses on these ash-liquid interactions and is therefore an original research.

Finally, as emphasized in the manuscript (e.g. P. 32538, L. 1; P 32541, L. 11), we focus on “plinian and sub-plinian eruption plumes”. This makes our work essentially dissimilar to the study mentioned by the reviewer (Martin et al. 2012), which investigated “quiescent eruption plumes” having no ash as a major player in the system (see also Martin et al 2010, Mather et al 2003 for more details). One should also note the difference in the mechanism of sulfate aerosol formation within these two distinct systems. While in “quiescent eruption plumes” homogenous nucleation of sulfate particles is the main particle growth mechanism (Martin et al. 2012), in presence of ash particles in “plinian and sub-plinian” plumes, such a mechanism is known to be unlikely (Textor et al. 2003). Instead, condensation of sulfuric acid on the ash surface is the main sulfate formation mechanism in such plumes (Textor et al. 2003, Tabazadeh and Turco, 1993). Water condensation and halogen uptake by such particles is accordingly different (Textor et al. 2003). Therefore, comparing the physical chemistry of “quiescent eruption plumes” with “plinian and sub-plinian eruption plumes” is obviously invalid.

Comment 2: The manuscript could also benefit from recognizing some of the extensive research on the topic of Fe solubilization in mineral dust, considered the globally dominant source of Fe to the ocean, which has laid much of the groundwork for the study of atmospheric processing of airborne Fe-bearing particles.

Reply: As explained above, the current work benefits from different methods and assumptions, which are developed and extensively used in various scientific disciplines including mineral dust research. For e.g., as mentioned in P. 32542, equation 1 which is the fundamental equation of the numerical model, is taken from studies on Fe solubilization in mineral dust (Meskhidze et al. 2005). For different parameters in this equation however, the original references in geochemistry and atmospheric sciences are cited (e.g. Palandri and Kharaka 2004, Blesa et al. 1994, Jacobson 2005).

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)



We note however that generalizing the atmospheric processing of airborne Fe-bearing particles and direct comparison of the ash and dust processing could be misleading. Volcanic ash and mineral dust are known to be dissimilar in terms of chemical, physical and mineralogical properties (Langmann 2013). Besides, volcanic ash plumes and clouds are extremely wet and acidic environments in comparison to the mineral dust clouds (Langmann 2013). Hence direct comparison between iron mobilizations processes affecting two dissimilar components within two distinct systems is not vigorous. Accordingly, despite of utilizing the methods presented in the mineral dust research, we avoid comparing our work with the results of the mineral dust studies. Nevertheless, we added few references concerning the dust studies (Desboeufs et al. 2001; Schroth et al. 2009; Journet et al. 2008; von der Hyden et al. 2012) to the introduction:

“Solubility of iron in airborne particles (e.g. mineral dust) is known to be strongly linked to its chemical speciation and mineralogy (Desboeufs et al. 2001; Schroth et al. 2009; Journet et al. 2008; von der Hyden et al. 2012). However, it is not yet fully understood which volcanic and atmospheric processes can modulate these properties within volcanic ash thereby modify the ash iron solubility.”

Comment 3: The initial ash mineralogy used in the model is unrealistic. In section 2.8, the authors state that “for simplicity, ash in this reference scenario consists of magnetite (Fe₃O₄) as the Fe-carrying mineral”. However, magnetite is far from being a dominant component of volcanic ash, let alone the only phase comprising ash. This represents a poor choice of “reference scenario”. Similarly, the sensitivity analyses performed in section 4.2 are based on highly unrealistic ash compositions. The authors consider a glass phase, as per Tables 2 and A3, devoid of all constituents other than Al, Si and O, with additions of 30% hematite, 30% fayalite, and 30% of mixed Fe-bearing phases (10% hematite, 10% fayalite, 10% magnetite). Volcanic ash never contains 10% magnetite, 10-30% hematite or 30% fayalite. Fundamentally, the authors utilize model ash systems which have no resemblance to actual volcanic ash. Hence, the comparisons they draw later within the paper are baseless: if the modelled systems have no resem-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

blance to volcanic ash, then the chance agreement between their predicted values and those of any real system lacks scientific relevance.

Reply: A short explanation is added to the revised MS (section 2.8 Initial ash and gas composition) to more clearly highlight the assumptions made for the ash composition (please see the added text after comment 5 below). We take this simplification as a limitation of the study but will show in the following lines that it does not affect the scientific significance of the results. We also elaborate the theoretical and experimental backgrounds of this assumption.

1- Scope of the study: We emphasize that this study does not intend to reproduce a particular data or situation at one volcano but to explore the role of in-plume processes in ash iron mobilization in general. As a commonly accepted routine in numerical modeling studies, one can simplify the system's components as far as the general behavior of the modeled system remains identical to the real system. This stems mainly from not only our limited understanding of the various components in the system but also the computational and numerical burdens. As a result, a numerical model does not intend to fully replicate all the components of the real-world system but to simulate its behavior in general (Jacobson 2005). Similarly, we reduce the complexities of the volcanic plume system by simplifying the volcanic ash composition. To validate this simplification, we evaluate if the system's general behavior (here the Fe release from the ash) is identical to that of the real world system.

2- Realistic vs. representative ash system (every real ash sample is unique in terms of composition): Several factors control the ash composition: magma composition and fragmentation, eruption mechanism etc. The great diversity and complexity of these factors in different eruptions result in extensive range of volcanic ash compositions (Nakagawa and Ohba, 2003, Ohba and Nakagawa 2003, Heinken 1972, Heinken and Wohletz 1992). Therefore, defining a fully realistic composition that can replicate all these complexities in different eruptions is not possible. A specific ash composition could be used only when a particular eruption is under consideration noting that the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



ash composition may change even during an eruption (Nakagawa and Ohba, 2003). This is not however the case in comparative studies like this MS. Comparative studies usually utilize ash systems that satisfactorily represent the general physicochemical behavior of the ash and not necessarily any real ash composition. For e.g. previous researchers have used synthetic ash which also fails to replicate the real ash composition but might show reasonable behavior in the system (Ayrís et al 2014, 2013). Therefore, the term “realistic ash composition” is vague and should be replaced by the term “representative ash behavior” or “idealized composition” instead, especially when it comes to the comparative and modeling studies.

3- There is a patent lack of data about the ash surface mineralogy and composition: Defining a representative ash composition is even more challenging in this study because we focus on the ash surface composition within few tens of nanometers at 600°C (Gislason et al 2011, Hoshyaripour et al. 2014). To our knowledge, there is a patent lack of data and study that directly resolve the chemical and mineralogical composition of this nanometer-scale rim. This includes the lack of data concerning iron mineralogy and speciation within this layer. Furthermore, as explained in the methodology, the initial conditions used in this study correspond to the ash surface composition at 600°C in the eruption plume before being affected by further in-plume and in-cloud processing. These facts further challenge the scientific relevance of comparing the composition used in this MS with observed ash bulk compositions or presenting a realistic composition for something that has not been directly measured so far.

4- Why is the fayalite-magnetite-hematite system used in this MS? As mentioned earlier, the initial ash mineralogy may seem unrealistic if one compares it with the ash bulk compositions reported in the literature (e.g. Nakagawa and Ohba 2003; Bayhorst et al. 1987). However this MS investigates the processes that occur at the ash surface affecting a rim with the thickness <100 nm (Gislason et al. 2011, Hoshyaripour et al. 2014). Ash surface composition is known to be incomparable with the bulk composition (Delmelle et al. 2007). This so-called salt layer at the ash surface is shown to be

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

the main reservoir for the immediate release of the elements upon contact with water (Achteberg et al., 2013) and is believed to be shaped mainly through the in-conduit, in-plume and in-cloud processes (Ayris and Delmelle 2012). The salt layer thickness on the ash from Eyjafjallajökull eruption, Iceland in 2010 is directly estimated to be 7 nm on average (Gisslasson et al 2011).

Despite the lack of data about the chemical and mineralogical composition of this nanometer-scale rim especially at 600°C (initial conditions in this MS), both experimental (Ohba and Nakagawa, 2003) and theoretical (Hoshyaripour et al., 2014) studies strongly suggest that iron oxidation state within this rim is mainly shaped through the high-temperature oxidation processes occurring in the eruption plume. Ohba and Nakagawa (2003) for example suggest that hematite is mainly produced in volcanic ash by oxidation and/or hydration of iron through interactions with water or ambient air during the eruption. Hoshyaripour et al. (2014) developed a conceptual model to explore such interactions at 600°C<T<1000°C. They suggested that a chain of oxidation reactions affect the 1-100 nanometers thick rim and convert the Fe²⁺-carrying minerals (e.g. fayalite Fe₂SiO₄) to Fe³⁺-carrying minerals (e.g. magnetite Fe₃O₄ and hematite Fe₂O₃). Fayalite is the first species in this chain mainly produced through magma crystallization/fragmentation and is extensively observed in volcanic ash samples (e.g. Censi et al., 2010; Bayhorst et al. 1987). It reacts with the ambient oxygen at T>800°C to produce magnetite. Magnetite is also observed in the ash compositions reported by many researchers (e.g. Censi et al., 2010; Bayhorst et al. 1987)). It could be oxidized to hematite at 600°C<T<800°C. Ohba and Nakagawa (2003) also suggest that hematite is mainly produced in volcanic ash by oxidation and/or hydration of iron through interactions with water or ambient air during eruption.

Progress of this reaction chain (that dictates the Fe oxidation degree at the ash surface) is however controlled by several factors like the retention time of the ash particles at T > 600°C, initial magma composition, ash/gas ratio, the amount of entrained ambient oxygen etc. Therefore, the iron mineralogy and oxidation state at the ash surface

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

could be represented by three end-members: fayalite as the non-oxidized, magnetite as moderately-oxidized and hematite as highly-oxidized (see Hoshyaripour et al. (2014) for more details). Magnetite is considered as the reference scenario because it has not only the intermediate iron redox state but also a dissolution rate close to the average of the dissolution rates of other possible ash components. We note again that this should not be directly compared with the well-documented data in the literature reporting the bulk mineralogy and composition of the volcanic ash, which is out of the scope of this study. Extensive experimental research is required to shed more light on the chemical and mineralogical properties of the volcanic ash surface focusing on nanometer scales. In conclusion, considering all these facts explained above (scope of the study, data availability and the scientific backgrounds) we are convinced that the assumptions made in this study concerning the ash initial composition are valid and robust. Comment 4: Additionally, by considering a glass devoid of all constituents other than Al, Si and O, the authors neglect two crucial factors in their model: i) the presence of Fe within the glass, and ii) the presence of other network modifying cations in the glass system. The authors argue that the Fe content of the ash's glassy component is negligible compared to Fe held in oxides and fayalite, and use this as a basis for neglecting Fe in glass altogether. I would like to see a rigorous calculation for this statement. Not only can Fe be present within the glass, but a fraction of this Fe will be 'soluble', as it is readily extractable via ion-exchange during aqueous leaching.

Reply: The answer to this comment could be found in the other comments made by the reviewer (for e.g. in the next comment). It is well-known that the glass dissolution involves three major steps 1) the relatively rapid removal of univalent and divalent cations; 2) aluminum releasing exchange reactions; followed by 3) the relatively slow detachment of partially liberated silica (Oelkers and Gislason 2001). In general, the higher the metal valence, the slower the dissolution rate at acidic conditions (Oelkers 2001). Thus, iron dissolves slower than the alkali and alkali-earth metals within the glass structure. In contrast, the acidic dissolution of the metal oxides (e.g. magnetite) (and also their corresponding orthosilicate minerals (e.g. fayalite)) involves breaking

only one metal-oxygen bond. Therefore, the mineral dissolution rate can exceed the glass dissolution rate at $\text{pH} < 2$ (Hamilton et al. 2000). Similarly, the iron release from the minerals is faster than that from the glass under acidic conditions. Figure 1 summarizes the dissolution mechanisms of some minerals and basaltic glass at acidic conditions. It is obvious from this figure that the mineral dissolution at acidic conditions is most likely more efficient than glass dissolution. For more details we refer the reviewer to Hamilton et al. (2000).

Comment 5: The proton consumption calculations in Table A3 neglect the influence of network modifying cations within the glass, despite the fact that in acidic solutions, these cations can be leached by ion exchange (thereby consuming protons) at higher rates than the rate at which the aluminosilicate network is dissolved. To exclude network modifying cations may artificially increase the duration of highly acidic conditions at the ash surface, and inflate the predicted Fe release. Network modifying cations must be included in order to reliably construct a model for simulating the chemistry of the acid solution reacting with volcanic ash.

Reply: We justified the simplifications concerning the ash composition and explained the scientific background above. The limitations due to these assumptions are discussed in the revised MS in a new section named “limitations”. Below, we present more details especially about the ash’s glassy component.

Dissolution rate in this study refers to “the steady-state temporal metal release rate divided by the stoichiometric number of moles of this metal in each mole of the dissolving mineral or glass” as defined by Oelkers (2001). In this context, steady state is defined as the conditions where dissolution is time independent and stoichiometric. This is the basis for the reported glass and mineral dissolution rates in the literature that are also used in this MS (e.g. Oelkers 2001, Oelkers and Gislason, 2001; Gislason and Oelkers, 2003 and the references therein). However, the process mentioned by the reviewer, i.e. the leaching of the network-modifying cations through ion exchange, is nonstoichiometric (Oelkers 2001). The question as to whether or not the stoichiomet-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

ric dissolution rates could be adopted to replicate the nonstoichiometric dissolution is difficult to answer, as to our knowledge no published studies have explicitly reported such nonstoichiometric dissolution reactions and their rates at $\text{pH} < 2$ and temperature below 25°C . Interestingly, recent scientific evidences strongly suggest that such a nonstoichiometric dissolution process is unlikely within a depth of few nanometers at the glass surface under acidic conditions (Helmann et al 2015).

The reviewer also criticized the glass composition used in table 3 because it lacks other glass constituents other than Al, Si and O. We note that this type of glass (hydrated glass) is extensively investigated over a wide range of pH and temperature (Hamilton et al. 2000; Oelkers and Gislason 2001, Gislason and Oelkers 2003, Wolff-Boenisch et al 2004; Flaathen et al. 2010). It is also the only glass for which we could find not only the dissolution rate as a function of pH but also the dissolution reaction, which are necessary components within the numerical model formulation explained in the MS. Moreover, as explained above, stoichiometric dissolution is a good approximation for the dissolution of hydrated glass as it lacks the alkali and alkali-earth metals that are involved in nonstoichiometric dissolution (Flaathen et al. 2010). Despite of the rich body of literature dealing with the natural glass dissolution (Oelkers 2001, Oelkers and Gislason 2001, Gislason and Oelkers 2003, Flaathen et al. 2010 and the references therein) a comprehensive data compilation to be used for geochemical modeling of glass dissolution remains lacking. We agree with the reviewer that the inclusion of a more complex glass in the model could be beneficial but our choice is limited currently by the data availability. In this sense our model explores one type of endmember case which is somewhat preferential towards the release of iron from mineral phases but nevertheless provides a very useful and novel insight in such complex systems. One direction for future works could be to compile the glass dissolution data (including both chemical reactions and the dissolution rates) as function of pH similar to the mineral dissolution data (Palandri and Kakhara, 2004). This will assist the future investigations in this field.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

To evaluate the role of alkali and alkali-earth metals in consuming protons during ash dissolution and perhaps limiting the iron mobilization, we conducted another sensitivity study. As discussed before, we did not find any data compilation that provides the reaction and the rates related to the step-wise release of cations from the glass through nonstoichiometric dissolution at $\text{pH} < 2$ and temperature below 25°C . Therefore, an alternative approach is used. Hamilton et al. (2000) showed that under acidic conditions the dissolution behavior of the minerals is identical to that of their corresponding glass. Therefore, here we use the minerals containing alkali and alkali-earth metals assuming that they behave identical to the glass in acidic solutions (Hamilton et al. 2000). The minerals are Albite ($\text{NaAlSi}_3\text{O}_8$), Enstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$), Wollastonite (CaSiO_3), Forstrite (Mg_2SiO_4) and Diopside (CaMgSiO_6). The dissolution rates of these minerals versus pH are obtained from Brantley (2004). The difference between dissolution rates may partly reflect the preferential dissolution of the metals within volcanic ash.

According to Bayhorst et al. (1987) we assume the following mineral assemblage in the ash: Albite 70 wt%, Enstatite 6 wt%, Wollastonite 6 wt% , Forstrite 6 wt% , Diopside 6 wt%, Fe-mineral 6 wt%. Similar to the MS, we replace the Fe-minerals here with fayalite, magnetite and hematite. We aim to compare the Fe release into the aqueous phase from ash containing all minerals+Fe-minerals with the Fe release from ash containing only Fe-minerals. This leads to 6 scenarios shown in table 1. It could be seen that the ash containing only Fe-minerals behaves nearly identical to the ash containing all other minerals in terms of iron release. In other words, despite the changes in the ash composition, the amount of Fe released into the aqueous phase remains nearly intact. This is could be explained by the following process: alkali and alkali-earth cations consume the protons and reduce the acidity of the liquid phase. This results in more efficient scavenging of HF and SO_2 , which compensates the loss of the protons through rapid dissociation. Therefore, more HF and SO_2 are scavenged in the scenarios where ash contains all minerals+Fe-minerals. We conclude that alkali and alkali-earth metals within volcanic ash can affect the ash dissolution behavior and its interaction with the gases and aerosols. But their impact of iron release into the aqueous phase is limited

to approximately 5-15%. In other words, by neglecting alkali and alkali-earth cations within the ash, we may slightly overestimate the iron mobilization. This indicates that the simplified proton consumption calculations used in the MS can reliably replicate the behavior of a real ash system containing alkali and alkali-earth metals. This sensitivity study is added to the revised MS.

To better clarify the assumptions concerning the ash initial conditions, this part of the MS is rewritten as below:

“Iron at the ash surface leaving the high-temperature zone mainly occurs as component of glass and as Fe-carrying phases (Bayhurst et al., 1991; Nakagawa and Ohba, 2003). Iron release from Fe-carrying minerals involves breaking only one Fe-O bond while in glass it may require breaking several metal-oxygen bonds through nonstoichiometric dissolution before reaching the steady state. (Oekler 2001) Furthermore, at pH<2 mineral may dissolve even faster than the corresponding glass (Hamilton et al. 2000). Considering this and given the limitation of data on nonstoichiometric iron release from the glass at pH<2 and T < 25°C, here we consider the minerals as the main source of iron within the ash particle and regard glass as a sink for protons (See Table 2). It is suggested that iron mobilization efficiency is connected to its redox state in the minerals (von der Hyden 2010, Desboeufs et al. 2001). To evaluate this hypothesis for volcanic ash we consider three redox end-members: fayalite as the non-oxidized, magnetite as moderately-oxidized and hematite as highly-oxidized Fe-carrying phases at the ash surface (see Hoshyaripour et al. (2014) for more details). Ash in this reference scenario consists of magnetite (Fe₃O₄) since it contains iron in both oxidation states (ferric and ferrous). It is also extensively observed in volcanic ash samples (Gislason et al. 2011, Censi et al., 2010; Bayhorst et al. 1987). The impacts of other minerals as well as silicate glass are discussed in a detailed sensitivity study in Sect. 4.2. We note that this composition refers to the composition of the ash surface rim with a thickness of <100 nm (Achteberg et al. 2013, Gislason et al. 2011, Hoshyaripour et al 2014). This rim undergoes substantial physiochemical interactions with gases and

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

aerosols within the plume and cloud that can eventually lead to generation of a salt layer on the ash surface (Achteberg et al. 2013, Gislason et al. 2011). This salt layer is suggested to be the main source of soluble iron in volcanic ash upon contact with sea water (Duggen et al 2010).”

Comment 6: In section 5.1, the authors claim that Figure 8 “unambiguously shows the higher the chlorine and fluorine concentrations, the lower the pH and the higher the iron release”. Figure 8 is constructed based on ash leachate data from Jones and Gislason (2008). However, Hoshyaripour et al. are wrong in their interpretation of these data. What they have plotted in Figure 8 correspond to time series leachate data obtained for individual ash samples. For each ash sample, the change in pH with time reflects consumption of protons during leaching and dissolution processes of the ash material. The decrease in sulfate and halide concentrations in ash leachates indicates rapid dissolution of sulfate and halide salts (Gislason et al. 2011). There is no relationship between these two separate processes, and the apparent trend observed is simply a product of the use of time series data, enhanced by the use of a log scale for the y-axis. Thus, Figure 8 is misleading and cannot be used to support the authors’ argument.

Reply: 1) We understand that plotting the whole time series might be confusing. Therefore, we removed the impact of time through plotting only 1 data point from each ash sample (after 50 minutes leaching taken from Jones and Gislason (2008)) corresponding to five different volcanic eruptions (Fig 2, left panel). It is evident that the correlation between pH, Fe and halide release still holds strongly, despite of removing the impact of the time from the plotted data. This proves the robustness of the argument made in the manuscript “the higher the chlorine and fluorine concentrations, the lower the pH and the higher the iron release”. Fig. 8 in the manuscript is replaced by Fig 2, left panel.

2) The reason why the Y axis is in logarithmic scale is the wide range of the values that are plotted. It could be seen that the difference between the values is up to 4 orders of magnitude. Plotting such a data on a linear axis makes it indistinguishable as it is

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



shown in Fig 2, right panel.

Comment 7: The authors should also exercise extreme caution in their comparisons between model output and leachate data. The authors make an assumption that 1-5% of the total ash mass is affected by dissolution, although the origin of this number must be cited or explained. Furthermore, the authors should then consider whether surface dissolution during leaching experiments conducted over a matter of hours at room temperature is capable of dissolving a similar mass fraction, to justify such a comparison.

Reply: We added the following explanation to the revised MS concerning the wt% of the ash surface being affected by dissolution:

“Considering both experimental (Gislason et al. 2011) and theoretical (Hoshyaripour et al. 2014) estimates concerning the thickness of ash surface layer, we assume the thickness of the ash rim to be on average 10 nm. Having a specific surface area of 1.1-2.1 m²/g (Delmelle et al, 2005), the surface rim in each gram ash with density of 2500 kg/m³ has the weight of approximately 0.01-0.05 g or 1-5% of the total ash mass.”

We agree with the reviewer that the direct comparison of the model outputs with the leachate data could be delicate. Therefore, as explained in the MS, we did not carry out such a direct comparison. We estimated the iron release from the ash using eq (3), in which only one term is taken from the model outputs (Di or wt% of the dissolved iron). This calculation results in a range for the moles of the iron that is mobilized in each gram ash during in-plume and in-cloud processes and could be potentially released later in contact with water. A short explanation is added to the revised MS to clarify this point.

Specific comments

P32536 lines 21-26: The connection between increased marine primary productivity in the ocean in 2008 and increased sockeye salmon in rivers in 2010 is not clear as

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



presented (the two effects are separated spatially and temporally) to those not familiar with the salmon life cycle. Furthermore, use of the salmon example to introduce the study seems to place the importance of ocean Fe fertilisation by volcanic ash in terms of impacts on ecology when the real importance of this process relates to impacts on atmospheric carbon dioxide drawdown and ultimately global climate, neither of which are mentioned by the authors.

Reply: We revised this part as below:

“In 2010, sockeye salmon unexpectedly reached record numbers in British Columbia’s Fraser River after low numbers during recent decades (Larkin, 2010). It has been hypothesized that the soluble iron contained in the volcanic ash from the eruption of Kasatochi volcano, Aleutian Islands, in 2008, could have indirectly provided a feast for the salmon (Parsons and Whitney, 2012) through an enhanced marine primary productivity (MPP) and phytoplankton bloom upon ash deposition into Fe-limited ocean surface waters (Olgun et al., 2013a). This phytoplankton bloom was indeed the first direct evidence of a fertilization effect of volcanic ash iron on the surface ocean (Langmann et al., 2010; Hamme et al., 2010). While small-scale ash iron fertilization events (e.g. after Eyjafjallajökull eruption in 2010, Iceland) trigger perturbations in the local marine biogeochemistry (Olgun et al., 2013b; Achterberg et al., 2013), large-scale events (e.g. the 1991 eruption of Mt. Pinatubo, Philippines) can stimulate the MPP and in turn, the atmospheric CO₂ drawdown globally (Sarmiento, 1993; Watson, 1997).”

P32537 lines 5-9: “knowing the fact that the ash Fe near the volcanic vent is mostly insoluble”. How exactly is this a known fact? It is an assumption by the authors based on the occurrence of Fe in ash in “the glass and as primary Fe-bearing silicate and Fe-oxide minerals”. Furthermore despite explicitly recognizing here these Fe-bearing phases in ash and acknowledging that processes which increase their solubility are poorly understood, the authors later (section 2.8) disregard both glass and primary Fe-bearing silicate minerals in their final model.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Reply: We substantially revised this part in the MS to better clarify this rationale of the study concerning the ash iron solubility.

“Upon eruption and near the volcanic vent, iron in the ash occurs mostly in non-soluble forms, i.e., in silicate glass and in primary Fe-bearing silicates and Fe-oxide minerals (Heiken and Wohletz, 1992, Schmincke, 2004). In the surface ocean however, the soluble species on the ash surface are suggested to be the main source of the iron affecting the ocean’s biogeochemistry (Hamme et al., 2010; Duggen et al., 2010; Achterberg et al., 2013). Solubility of iron in airborne particles (e.g. mineral dust) is known to be strongly linked to its chemical speciation and mineralogy (Desboeufs et al. 2001; Schroth et al. 2009; Journet et al. 2008; von der Hyden et al. 2012). However, it is not yet fully understood which volcanic and atmospheric processes can modulate these properties in volcanic ash thereby modify the ash iron solubility.”

P32537 lines 14: Fragmentation of what?

Reply: this term is replaced by “magma fragmentation”.

P32538 lines 10-13: I don’t understand this statement. Did the authors calculate the amount of iron chloride salts formed in Ayris et al. (2014)’s experiment? How?

Reply: The following sentence is from Ayris et al. (2014): “The primary reaction product formed during adsorption is halite (NaCl), in addition to minor quantities of Ca-, K-, Al- and Fe-bearing chlorides.” Ayris et al. (2014) admit that iron chloride it is in “minor quantities” but do not provide any quantitative measure that can be used to estimate the amount of iron chloride salt formed in the experiment. Therefore, it is difficult to evaluate their claims concerning the iron chloride formation in volcanic ash due to high-temperature processes and its relevance to ocean fertilization. It is also very unlikely that this soluble iron chloride remains intact within the ash upon atmospheric transport as several processes within the volcanic plume and cloud most likely affect it (Ayris and Delmelle 2012).

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

P32537 lines 17-20: I don't understand this sentence, confusing.

Reply: the sentence is rewritten as follow in the revised MS:

“During the transport from the magma fragmentation to high altitudes in the atmosphere and finally to the surface ocean, physicochemical properties of volcanic ash could be altered by several processes occurring within the conduit, plume and cloud (Table 1).”

P32537 lines 23-26: Bagnato et al. (2013) did not determine the surface composition of Eyjafjallajökull's ash; they reported the concentrations of dissolved elements in ash leachates. They tentatively interpreted the differences in ash leachate compositions in terms of enhanced volcanic ash-gas interaction during transport downwind. Based on this, they calculated in-plume/cloud ash dissolution and salt formation rates. However, Delmelle et al. (2014) showed in a later comment that Bagnato et al. (2013)'s calculations were incorrect. Bagnato et al. partly acknowledged this flaw (Bagnato et al. 2014).

Reply: We followed, with much interest, the comment and reply mentioned above. As far as we know, Bagnato et al.(2014) proved that their experimental method and the reported leaching data are valid. They only miscalculated the ash dissolution rates in the cloud which does not affect the validity of the rest of their work. This part in the MS is rewritten as below:

“For instance, Bagnato et al. (2013) observed a significant difference between ash leachate compositions of proximal and distal ash deposits of Eyjafjallajökull eruption in 2010, Iceland. These alterations in the ash leachate composition are attributed to the in-plume and in-cloud processing of volcanic ash during transport downwind (Bagnato et al., 2013).”

P32538 line 3: Post-fragmentation of what?

Reply: Post-fragmentation of magma

P32538 lines 6-10: Here, the authors mention two processes, SO₂ scavenging by a

C13272

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Ca²⁺ diffusion-driven mechanism and Fe-bearing salt formation after HCl adsorption, which both require cations sourced from silicate glass as used by Ayris et al. in the cited studies (2013; 2014). However, later (section 4.2) Hoshyaripour et al. not only discount glass as a potential source of Fe but furthermore choose a glass composition bearing none of the other network modifying cations typically present in volcanic glass, e.g., Ca, Mg, Na, K.

Reply: Please see the answers to the general comments above

P32538 lines 20-21: What is the rationale for defining these three zones within an eruption plume? What dictates the cut-offs?

Reply: The details are clearly presented in Table 1 and Fig 1. We should note that, as mentioned in the MS, these zones could overlap especially at the boundaries. Therefore, there are no sharp cut-offs in the system.

P32539 line 3: It is not a “procedure” but a process.

Reply: ‘Procedure’ is replaced by “process” in the revised MS.

P32539 lines 8-10: As far as I know Ayris and Delmelle (2012) make no mention of freezing/melting processes in relation to Fe salt generation.

Reply: Ayris and Delmelle (2012) is not cited in the MS for this process. As one can see in P32539 line 7-8, freezing/melting is mentioned as an example of the in-cloud processes according to Duggen et al (2010) and not Ayris and Delmelle (2012).

P32539 lines 18: How do the authors know that these atmospheric processes increase ash iron solubility? Please provide a reference.

Reply: the sentence is rewritten as follow in the revised MS:

“As a result, despite of advancements made by individual studies, a detailed insight into the in-plume and in-cloud processes that could promote the iron mobilization in volcanic ash remains lacking.”

P32539 lines 21-22: The first main objective mentions assessing ferrous and ferric iron. However, there has been no previous mention regarding the importance of distinguishing the specific redox states of Fe released from ash (e.g., in the context of ocean fertilisation).

Reply: According to the previous comments, we added a short explanation to the introduction concerning the effect of redox state on solubility.

“Solubility of iron in airborne particles (e.g. mineral dust) is known to be strongly linked to its chemical speciation and mineralogy (Desboeufs et al. 2001; Schroth et al. 2009; Journet et al. 2008; von der Hyden et al. 2012).”

P32539 lines 22-23: It is claimed here that the study focuses on processes within the vertical eruption plume. However, later the authors discuss processes within the volcanic cloud, which corresponds to the horizontal transport of the volcanic gas-ash mixture in the atmosphere. Please clarify.

Reply: As indicated in Table 1 and Fig 1 in the MS, this study does not differentiate the plume and cloud based on vertical and horizontal transport. Such a criterion is indeed misleading as for e.g. vertical transport occurs within convective clouds in the atmosphere but they are still classified as clouds (Jacobson 2005). The main criterion that we suggest here is based on water condensation. In other words, the zone within the vertical column that contains condensed water vapor (and ice particles later) is considered as cloud. The rest is defined as plume. Please refer to Table 1 and Fig 1 for more details.

P32540 line 21: Fe³⁺ is also released upon leaching/dissolution of the ash material.

Reply: Fe³⁺ is added to the revised MS

P32540 line 22: “. . .can react with each other generating soluble salts”, such as?

Reply: This sentence is rewritten as below in the revised MS:

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

“These processes release cations (e.g., Na⁺, Fe³⁺, Fe²⁺, Al³⁺) and anions (e.g., Cl⁻, SO₄⁻², F⁻) into the liquid phase, which can react with each other through aqueous chemistry generating soluble salts such as NaCl and FeCl₂ (Stum and Morgan, 1996).”

P32540 lines 20-22: Here again it is explicitly stated that dissolving constituents of the ash surface, releasing cations such as Na⁺, Fe²⁺ and Al³⁺, leads to generation of soluble salts with Cl⁻, SO₄²⁻ and F⁻, yet the most likely source of these cations (i.e., the silicate network) is later eliminated from the final model scenario.

Reply: Please refer to the answer to the major comments 3, 4 and 5 above.

P32540 lines 24-25: It has been suggested that for eruptions, which inject a plume high into the atmosphere, the ash particles are quickly coated with ice. This phenomenon may not leave enough time for efficient ash-liquid water interactions. Can the authors comment on this in the context of their study?

Reply: As it is mentioned in the MS (P32541), it has been shown previously that the presence of ions in the liquid phase cause a depression in saturation vapor pressure and shift the freezing point to lower temperatures leading to super-cooled water formation (Tabazadeh and Turco, 1993, Textor et al 2003). Textor et al 2003 suggest -40°C as the water freezing point within the plinian eruption plumes. Since we do not reach subzero temperatures in the context of this study (please see Fig 1 for the temperature ranges), ice formation is unlikely within the zones that we simulate here.

P32541 line 11: The ACP audience may not be familiar with the terms Plinian and sub-Plinian. Please define or use other wording.

Reply: The definition is added to the revised MS.

P32541 line 14: The temperature of a rhyolitic magma is 650-800 °C. How can the gas-and-ash plume generated by a rhyolitic eruption be cooled by 1000 °C upon entry into the atmosphere?

Reply: As explained in the MS, this is a first order approximation based on 1D eruption

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

plume models. Such models suggest an average plume rise time of 200 s for a wide range of initial conditions (Hort and Garner, 2000). For rhyolitic magmas this means a cooling rate of 3.2–4 C/s that is very close to the range we suggested in the MS (4–7 C/s). As mentioned in the MS, the results are not sensitive to the variation of this particular parameters.

P32543 lines 6–7: The authors mention here that it is the dew point of the acid gas mixture which needs to be considered. However, later they calculate and use the dew point of H₂SO₄ only (Appendix A1) and not that of the SO₂+HCl+HF gas mixture. Can the authors clarify this assumption (see also Appendix A1).

Reply: Dew point of pure H₂SO₄ is approximately 337 C, which is significantly higher than that of pure water (100 C), SO₂ (-10 C), HCl (-85 C) and HF (19.5C). Therefore it condenses first in the mixture followed by water condensation. In the atmospheric environment and in presence of liquid water, direct condensation of the gases with very low dew points (e.g. SO₂, HCl and HF) is very unlikely compared to that of sulfuric acid (Seinfeld and Pandis 2006).

P32544 line 6: Fe²⁺ and Fe³⁺ are not “formed”, they are released. Where is this Fe²⁺ and Fe³⁺ coming from, which Fe-bearing phases?

Reply: This sentence is rewritten as below in the revised MS:

“This dissolution process eventually results in release of Fe²⁺ and Fe³⁺ from Fe-carrying species into the aqueous phase (together with other cations and anions). This is central to further in-cloud processing of volcanic ash as the dissolved ions can play a significant role in cloud aqueous chemistry. “

P32544 line 7: Why is it “. . . central to further in-cloud processes”. Please expand.

Reply: Please see the revised sentence in previous comment.

P32544 lines 13–16: The choice of particle size (<1 mm) by the authors is partly because they “can be lifted to high altitudes and remain suspended in the atmosphere for

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

several days before sedimentation”. Presumably, this is relevant in terms of considering ash particles which may eventually be carried to the ocean and induce fertilisation. However along the same lines the authors do not consider that with a decrease in the size of ash particles that remain suspended in the atmosphere for several days, there is also typically a corresponding shift in mineralogy to a higher proportion of glassy particles due to faster sedimentation of heavy crystalline minerals, including magnetite (Hinkley et al. 1982). Therefore the authors’ later choice of a purely magnetite ash in the model is unlikely to be representative of a particle which might be carried 100s to 1000s km to the open ocean.

Reply: The reviewer is correct. But we note that magnetite is not the only component considered in the MS. There are also sensitivity study scenarios in the MS where 70-100% of the ash is glass. The “representative” ash composition is most probably somewhere between these two end-member cases. For more explanations about the ash composition, please refer to the answers to the general comments above.

P32545 line 16: “. . .more likely”, more likely than what?

Reply: This sentence is rewritten as below in the revised MS:

“It is known that plinian and subplinian eruptions are more likely within convergent plate volcanism than other tectonic systems (Schmincke, 2004). “

P32545 lines 24-27: “Iron at the ash surface leaving the high-temperature zone mainly occurs as component of glass and as Fe-carrying phases mentioned in Table 2”. However, the glass composition provided in Table 2 does not include Fe (or any other cations found in volcanic glass; Mg, Ca, Na, K, etc.). Furthermore, the authors explicitly acknowledge glass as a main source of Fe but then directly follow on to state that “for simplicity, ash in the reference scenario consists of magnetite”. This is confusing and contradictory.

Reply: For more details about consistency of the assumptions made in this study,

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

please see the answer to the general comments above. The text is rewritten to clarify the simplifications concerning ash initial composition. Please see the added text after general comment 5 above.

P32546 lines 2-3: “Its presence in volcanic ash is also reported in analytical studies” (referring to magnetite), but certainly not in the quantities modelled by the authors. Please provide a justification or suitable reference in support of this choice.

Reply: Please see the reply to the previous comment and also the detailed explanations addressing the major comments 3, 4 and 5 above.

P32548 line 11: Delmelle et al. (2007) did not carry out an experimental study and did not report dissolution rates for magnetite. They tentatively inferred ash dissolution rates based ash leachate and surface composition analyses. Please revise.

Reply: This sentence is rewritten as below in the revised MS

“The acidic liquid phase ($\text{pH} < 0.5$) dissolves the ash with an average dissolution rate of $6.44 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$, which is in the range of ash dissolution rates reported in pervious studies (Delmelle et al., 2007).”

P32548 lines 11-16: Again the other cations which may be released (Ca, Mg, Na, K) are ignored despite their role in consuming H^+ as well. This leads to errors in calculations of the acidity as well as the salts generated during this dissolution process.

Reply: Please refer to the answer to the major comments 3, 4 and 5 above.

P32548 lines 15-16: Hoshyaripour et al. corroborate some of their results based on over- or misinterpretation of previous studies on volcanic ash. For example, the statement that “ash particles are coated by a thin layer of salts in the form of iron sulfates and iron halides in the eruption plume” is supported by Naughton et al. (1974) and Delmelle et al. (2007) is incorrect. These papers do not report the observation of such salts. As far as I know Fe salts have never been directly observed at the surface of ash.

Reply: This part is revised as below:

“This is supported by the observation of a thin layer of salts on volcanic ash surface containing chlorine, fluorine and sulfate together with iron, alkali and alkali-earth metals (Naughton et al. 1974, Delmelle et al. 2007, Gislason et al. 2011)”

P32548 line 17: Confusing. What is “0.15% of the total surficial magnetite”? Is this assuming the whole particle is magnetite? Then what is the definition of the surface (i.e., what depth?). Please clarify.

Reply: Please see above for the clarifications that are added to the revised MS.

P32548 lines 18-20: This statement should be clarified. It is not clear what exactly the authors want to say.

Reply: The text is rewritten as below in the revised MS:

“This small wt% quantity may seem negligible. But if one takes into account the huge mass of ash that usually erupts during major eruptions (several mega tones), a tiny portion of that material has already a sizable mass. This is further discussed in Sect. 5.1.”

P32548 lines 23-24: This subdivision of ash composition based on tectonic setting is oversimplistic since ash composition within a given tectonic setting can vary substantially. This classification, inherited from a previous paper by Olgun et al. (2011), is misleading.

Reply: As the title and also the text of this section indicate, we subdivide the gas composition (and not the ash) based on tectonic setting. For more details concerning the distinct composition of the gas erupted from different tectonic settings please refer to Symonds et al., 1994 and the references there in. To avoid confusion, we replaced the tectonic settings convergent plate, divergent plate and hot spot with halogen-rich, carbon-rich and sulfur-rich magmatic gases in the revised MS.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P32549 line 19: “. . .considerable amounts of silicate glass”. This is rather vague. Please give range of crystallinity.

Reply: The range of crystallinity is mentioned in the revised MS. In explosive volcanic eruptions, the crystal fraction is in the range of 20-60% (Blundy et al 2006).

P32550 line 19: How can SO₂ dissociate and give off a proton?

Reply: According to the following reaction which is also mentioned in Table A2 (Jacobson, 2005):



P32550 line 19: HF is a weak acid (pK_a 3.14) and will barely contribute to the acidity of a H₂SO₄-HF solution. Please revise.

Reply: Although HF is generally weaker than H₂SO₄, one should also note their quantities in the system. The HF concentration in the initial gas composition (Table 3) is up to 1 order of magnitude higher than that of H₂SO₄. Moreover, these are not the only species that contribute to the acidity of the aqueous phase. Please refer to Table A2 for the list of the reactions that can release protons in the aqueous phase. We note that the chemical principals (like the one mentioned by the reviewer concerning pK_a) are the underlying basics of the chemical and thermodynamic reactions (and their rate parameters) considered in this study.

P32551 lines 3-4: What is the basis for this statement? The authors are not comparing acid-mediated release of Fe from ash to any of the volcanic/atmospheric processes susceptible to increase ash Fe solubility.

Reply: The statement reads as follow: “Based on the results presented above, acid-mediated dissolution of the ash seems to be the major process that mobilizes the ash iron.” This is a hypothesis derived from the results and is evaluated later in this section through comparison with observations.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

P32551 line 7: The role played by fluoride in increasing the dissolution rate of silicates is linked to the formation of aqueous Al-F complexes which decrease the Al concentration in solution, therefore driving the dissolution reaction to the right. It is not related to pH of the solution. See Wolff-Boenisch et al. (2004).

Reply: As clarified in the MS and also above, aqueous chemistry is beyond the scope of this work. In other words, formation of cation-anion bounds in the aqueous phase is not simulated in this study and is therefore irrelevant to the interpretation of our results. Wolff-Boenisch et al. (2004)

P32551 lines 16-17: “. . .unhydrated volcanic ash samples”. There is always water adsorbed onto ash surfaces, ash cannot be unhydrated.

Reply: The term “unhydrated ash” is taken from Jons and Gislason (2008). Please refer to this paper for more details.

P32551 lines 17-18: Some of the ash samples used by Jones and Gislason (2008) may not be purely magmatic (for example, the ash from Sakurajima and Galeras). They may contain hydrothermal minerals, including gypsum and halite eroded from the volcanic conduit during the eruption. Jones and Gislason (2008) did not report the mineralogy of their ash samples. At least, this should be evoked.

Reply: A short explanation is added to the revised MS to address this point.

P32553 line 1: “This confirms the strong connection between iron release from ash with the halide concentrations and pH.” I doubt very much so.

Reply: Please see the answer to the major comment 6 and also Fig 3 above.

P32555 lines 13-19: This is a huge leap from talking of Fe release from volcanic ash to then “injection of volcanic gases into the stratosphere and its climatic impacts”. The authors make no clear connection between these processes and it does not seem appropriate in the conclusions and implications for this study.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Reply: This study shows, for the first time, how the HCl, SO₂ and HF scavenging by volcanic aerosols could be influenced by the proton consumption through ash dissolution. This point is added to the revised manuscript to better demonstrate the connection between these processes:

“The local, regional and global impacts of volcanism upon the Earth system (atmosphere, hydrosphere, pedosphere, cryosphere and biosphere) are initially induced by the physicochemical properties of the ash and gas. Several lines of evidence indicate that the in-plume and in-cloud processes can significantly alter these properties and thus, their impacts on Earth system. For instance, the efficiency of HCl, SO₂ and HF scavenging by volcanic aerosols could be influenced by the proton consumption through ash dissolution. This can modulate the amount of the volcanic gases that reach the middle atmosphere. Therefore, the in-plume and in-cloud processing of the volcanic ejecta need to be considered in future investigations on, for e.g., injection of volcanic gases into the stratosphere and its climatic impacts.”

Section 6 – Conclusions: The study is framed from the beginning with the purpose of better understanding the processes controlling Fe release in volcanic ash yet this thread seems lost in the conclusion which rather reads as a jumble of ideas surrounding factors influencing Fe in ash in volcanic plumes and potential impacts of ash emissions on the Earth System. Furthermore, the importance of this as an area of research is overwhelmingly in terms of the potential impact of ocean Fe fertilisation by volcanic ash on atmospheric carbon dioxide concentrations and thereby, on global climate, which the authors altogether fail to acknowledge.

Reply: To address this comment, the conclusion section is rewritten. Please see above.

Appendices A1 and A2 – Several abbreviations are defined although they do not appear in the equations shown. Please double-check.

Reply: We carefully checked the appendices. All defined abbreviations are used in the equations.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

References:

Achterberg, et al (2013), Natural iron fertilization by the Eyjafjallajökull volcanic eruption, *Geophys. Res. Lett.*, 40, 921–926, doi:10.1002/grl.50221

Ayris, et al (2014) HCl uptake by volcanic ash in the high temperature eruption plume: mechanistic insights, *Geochim. Cosmochim. Ac.*, 144, 188–201, doi:10.1016/j.gca.2014.08.028

Ayris, et al (2013) SO₂ sequestration in large volcanic eruptions: high-temperature scavenging by tephra, *Geochim. Cosmochim. Ac.*, 110, 58–69

Ayris and Delmelle (2012) Volcanic and atmospheric controls on ash iron solubility: a review, *Phys. Chem. Earth*, 45–46, 103–112.

Bayhurst et al (1991) A method for characterizing volcanic ash, in: *Volcanic ash and aviation safety: Proceedings of the First International Symposium 5 on Volcanic Ash and Aviation Safety*, p. 16, USGS

Blesa et al (1994) *Chemical Dissolution of Metal Oxides*, CRC Press, 1994.

Bobrowski et al (2007) Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res.-Atmos.*, 112, D06311, doi:10.1029/2006JD007206

Brantley S (2004) Reaction Kinetics of Primary Rock-forming Minerals under Ambient Conditions *Treatise on Geochemistry* 11/2003; 5:73-117. DOI: 10.1016/B0-08-043751-6/05075-1

Censi et al (2010) Trace element behaviour in seawater during pyroclastic Etna's activity in 2001. Concurrent effects of nutrients and formation of alteration minerals. *J Volcanol Geoth Res* 193(1-2):106-116.

Delmelle et al (2005) Surface area, porosity and water adsorption properties of fine volcanic ash particles, *B. Volcanol.*, 67, 160–169

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Desboeufs et al. (2001) Factors influencing aerosol solubility during cloud processes. *Atmos. Environ.* 35(20): 3529-3537.

Flaathen et al (2010) The effect of aqueous sulphate on basaltic glass dissolution rates, *Chem. Geolo.* 277, (3–4) 345-354.

Gislason et al (2011) Characterization of Eyjafjallajökull volcanic ash particles and a protocol for rapid risk assessment. *Proceedings of the National Academy of Sciences of the United States of America.* 108(18):7307-7312. doi:10.1073/pnas.1015053108.

Gislason and Oelkers (2003) Mechanism, rates and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochim. Cosmochim. Acta* 67, 3817–3832.

Hamilton et al (2000) Dissolution of albite glass and crystal. *Geochim Cosmoch Ac* 64:2603-2615.

Hoshyaripour et al (2014) High temperature volcanic controls on ash iron solubility: new insights from high-temperature gas–ash interaction modeling, *J. Volcanol. Geoth. Res.*, 286, 67–77.

Heiken and Wohletz (1992) *Volcanic Ash*, University of California Press, London,

Heiken (1972) *Morphology and Petrography of Volcanic Ashes*, Geological Society of America Bulletin, v. 83, p. 1961-1988

Helmann et al (2015) Nanometre-scale evidence for interfacial dissolution–reprecipitation control of silicate glass corrosion *Nature Mater.* 14, 307–311.

Jacobson (2005) *Fundamentals of Atmospheric Modeling*, Cambridge University Press

Journet et al. (2008): Mineralogy as a critical factor of dust iron solubility. *Geophys. Res.Lett.* 35, doi:10.1029/2007GL031589.

Jones and Gislason (2008) Rapid releases of metal salts and nutrients following the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

deposition of volcanic ash into aqueous environments, *Geochim. Cosmochim. Ac.*, 72, 3661–3680,

Langmann B. (2013) Volcanic ash versus mineral dust: atmospheric processing and environmental and climate impacts, *ISRN Atmospheric Sciences*

Martin et al (2012) The uptake of halogen (HF, HCl, HBr and HI) and nitric (HNO₃) acids into acidic sulphate particles in quiescent volcanic plumes. *Chemical Geology* 296–297, 19-25.

Mather et al (2003), Size-resolved characterisation of soluble ions in the particles in the tropospheric plume of Masaya volcano, Nicaragua: Origins and plume processing, *Journal of Atmospheric Chemistry*, 46, 207-237

Meskhidz et al (2005): Dust and pollution: a recipe for enhanced ocean fertilization?, *J. Geophys. Res.-Atmos.*, 110, D03301, doi:10.1029/2004JD005082

Nakagawa and Ohba (2002) Minerals in volcanic ash 1: primary minerals and volcanic glass, *Global Environmental Research*, (6) 41–51,

Oelkers (2001) General kinetic description of multioxide silicate mineral and glass dissolution. *Geochim. Cosmochim. Acta* 65, 3703–3719.

Oelkers and Gislason (2001) The mechanism, rates and consequences of basaltic glass dissolution: I. An experimental study of the dissolution rates of basaltic glass as a function of aqueous Al, Si and oxalic acid concentration at 25 °C and pH=3 and 11. *Geochim. Cosmochim. Acta* 65, 3671–3681.

Ohba and Nakagawa (2002), Minerals in volcanic ash 2: secondary minerals *Global Environmental Research*. 6(2). 53-59

Palandri and Kharaka (2004) A Compilation of Rate Parameters of Water–Mineral Interaction Kinetics for Application to Geochemical Modeling, USGS.

Schroth et al. (2009): Iron solubility driven by speciation in dust sources to the ocean.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Nature Geosciences, 2(5): 337-340.

Seinfeld and Pandis (2006) Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley and Sons, New York, 32540, 32571

Sigmarsoon et al (2013) The sulfur budget of the 2011 Grímsvötn eruption, Iceland, GEOPHYSICAL RESEARCH LETTERS, VOL. 40, 6095–6100

Tabazadeh and Turco (1993) Stratospheric chlorine injection by volcanic eruptions: HCl scavenging and implications for ozone, Science, 260, 1082–1086.

Textor et al (2003) Injection of gases into the stratosphere by explosive volcanic eruptions, J. Geophys. Res.-Atmos., 108, 4606.

Wolff-Boenisch et al (2004) The dissolution rates of natural glasses as a function of their composition at pH 4 and 10.6, and temperatures from 25 to 74 °C. Geochim. Cosmochim. Acta 68, 4843–4858.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 32535, 2014.

ACPD

14, C13256–C13289,
2015

[Interactive
Comment](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

[Discussion Paper](#)

C13286



Reaction	Feldspar	Anorthite	Muscovite	Estatite	Wollastonite	Olivine	Oxides	Basaltic Glass
Alkali metal –H exchange	Step 1 ↓	↓ Step1 ↓	Step 1 ↓	↓ Step 1 ↓	↓ Step 1 ↓	↓ Mineral destroyed	↓ Oxide destroyed	Step 1
Ca–H exchange								Step 2
Mg–H exchange								Step 3
Al–H exchange	Step 2	Mineral destroyed	Step 2	↓	↓			Step 4
Breaking Si–O bounds	Mineral destroyed		Mineral destroyed	Mineral destroyed	Mineral destroyed			Solid destroyed

Fig. 1. Fig 1: Summary of dissolution mechanisms of some minerals and basaltic glass at acidic conditions (Oelkers 2001)

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

[Interactive
Comment](#)

Ash Composition		pH	Scavenged	Scavenged	Fe in aq mole/cm ³	Difference %
			SO ₂ %	HF %		
Minerals + -	Fayalite	1.45	22.88	66.41	1.98E-08	
	Fayalite	1.35	19.48	61.48	2.32E-08	+14.43
Minerals + -	Magnetite	0.53	4.12	19.06	4.11E-10	
	Magnetite	0.32	2.86	12.78	4.41E-10	+6.85
Minerals + -	Hematite	0.52	4.04	18.70	3.59E-11	
	Hematite	0.32	2.82	12.59	3.85E-11	+6.78

Fig. 2. Table 1: Sensitivity of Fe-mobilization to the ash mineralogical composition[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

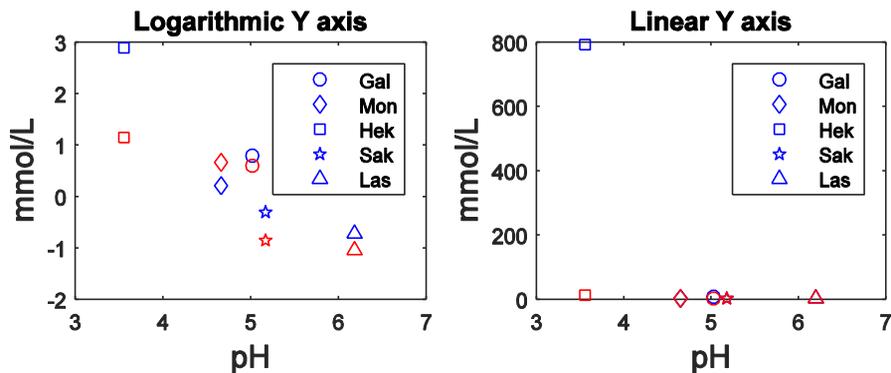
[Interactive
Comment](#)

Fig. 3. Fig 2: Fe (blue) and halide (red) release from the individual ash samples as a function of pH after 50 minutes leaching.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)