

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

P. Delmelle (Referee)

pierre.delmelle@uclouvain.be

Received and published: 12 February 2015

The study by Hoshyaripour et al. investigates the volcanic processes which may enhance the solubility of iron (Fe) in volcanic ash, thereby potentially explaining the capacity of ash to promote phytoplankton growth upon deposition in oceanic areas where Fe is a limiting micronutrient. To this end, the authors develop a one-dimensional model to simulate gas-ash-aerosol interactions within volcanic eruption plumes. They compare their model outputs with laboratory results reported in previous ash leaching studies. The authors conclude that HCl in volcanic gases largely controls the acidity of the gas condensate produced upon cooling of the eruption plume. The low pH condensate then promotes rapid dissolution of the Fe-bearing compounds in ash particles.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

The authors also claim that dissolution of Fe in ash is more effective when Fe occurs as ferrous iron (Fe(II)). The research topic may appeal to the scientific community interested in atmospheric deposition and ocean biogeochemistry.

I have found Hoshyaripour et al.'s paper confusing and contradictory in places. The English also requires editing. More importantly, the paper contains serious scientific issues. The selected input parameters for their model are flawed and consequently, the results cannot be considered comparable to the system they envisage to simulate. This, and additional errors in the interpretation of existing data or literature, compromises the conclusions and the validity of their paper. 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 relationship 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). 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.

Overall, Hoshyaripour et al.'s paper does not provide a rigorous quantification of the amount of Fe (and other elements) that may be solubilized upon interaction between the ash particles and acidic gas condensates in volcanic plumes/clouds.

General comments

1) 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

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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”.

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

3) 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.

4) 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

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Printer-friendly Version

Interactive Discussion

Discussion Paper



reacting with volcanic ash.

5) 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.

6) 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.

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 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

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Discussion Paper



are mentioned by the authors.

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.

P32537 lines 14: Fragmentation of what?

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?

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

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).

P32538 line 3: Post-fragmentation of what?

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

Full Screen / Esc

Printer-friendly Version

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Discussion Paper



bearing none of the other network modifying cations typically present in volcanic glass, e.g., Ca, Mg, Na, K.

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

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

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.

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

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).

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.

P32540 line 21: Fe^{3+} is also released upon leaching/dissolution of the ash material.

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

P32540 lines 20-22: Here again it is explicitly stated that dissolving constituents of the ash surface, releasing cations such as Na^+ , Fe^{2+} and Al^{3+} , leads to generation of soluble salts with Cl^- , SO_4^{2-} and F^- , yet the most likely source of these cations (i.e., the silicate network) is later eliminated from the final model scenario.

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

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Discussion Paper



may not leave enough time for efficient ash-liquid water interactions. Can the authors comment on this in the context of their study?

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

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?

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).

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

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

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 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.

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

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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:

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.

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.

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.

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.

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.

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

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.

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

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

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.

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.

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).

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

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.

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

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.

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.

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

Additional references

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