

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

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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.

Comment 1: The presented results are, in my opinion, limited in terms of new findings and correspond rather to a methodological paper on the development of 1-D model. In session 3 and 4, there is a lack of comparisons between results and references to support the reliability of the study. The text needs to be clarified and corrected to improve the original aspects of the paper for publication. Even if the purpose of this study is the estimation of atmospheric volcanic iron fluxes to the Ocean, it is an upstream

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work focusing on volcanic physico-chemical processes, which will be rather adapted to a journal on Earth problematic (as the majority of cited journal in the references)?

Reply: In general, a numerical model does not necessarily produce new concepts or laws. 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”.

The model presented in this study considers, for the first time, volcanic ash as a chemically active agent in the eruption plume. Its approach in simulating the gas-ash-aerosol interaction is also novel and leads to original findings. For instance, it demonstrates how 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 and thus their climatic impacts. Therefore, this study sheds more light on the impacts of in-plume and in-cloud processing on not only the ash iron mobilization but also the gas scavenging efficiency by aerosols within the eruption plume.

As mentioned above, this interdisciplinary research assimilates different methods and assumptions, which are developed and extensively used in various scientific disciplines. However, atmospheric chemistry and physics is the main stream of the methodology used in this paper (>90% of the processes). The results have also significant

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implications for the atmospheric science community for e.g. to better comprehend the fate of the volcanic emissions in the atmosphere and their climate impacts. Therefore, despite of its multidisciplinary nature, we regard this MS fully within the scopes of the ACP journal.

Comment 2: The title is very general and needs to be changed, e.g. “Investigation on the physicochemical processes implied on ash iron mobilization in volcanic eruption plumes (by 1-D modelling)”.

Reply: Based on this comment, the title is revised as follow: “Modeling the iron mobilization through the physicochemical processing of volcanic ash within eruption plumes”

Comment 3: 32537 L5: It is mentioned that “iron near the volcanic vent is mostly insoluble”, that means? Several studies on the solubility of fresh volcanic ash (< 1 or 2 hours) show that Fe ash has a very low solubility but is as soluble as dust Fe and that solubility seems to decrease with the age of volcanic ash, so probably with the distance to the source (e.g. Olgun et al., 2011). Mostly insoluble vs low solubility: what is the order of magnitude? Is it really this difference of solubility which can explained the fertilizing role of volcanic ash? Or simply the large deposition of volcanic particles (as developed in your paragraph p32553 L3). Please develop these points to support the rationale of the study.

Reply: As suggested by the reviewer, we revised this part in the MS to better clarify the rationale of the study:

“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 altering the ocean’s biogeochemistry [Hamme et al., 2010; Duggen et al., 2010; Achterberg et al., 2013]. Solubility of iron in airborne particles is known to be strongly linked to its chemical speciation and mineralogy [von der Hyden et al. 2012]. However, it is not

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yet fully understood which volcanic and atmospheric processes can modulate these properties thereby modify the ash iron solubility.”

Comment 4: 32539 L9: It is known for other mineral particles, in particular dust, that cloud processing, acidification, mineralogical composition. . . are major parameters playing on iron solubility (e.g. Desboeufs et al., 2001; Hand et al, 2004; Schroth et al., 2009). I think that this literature should be mentioned in the background session then discussed in comparison of your results.

Reply: The suggested literature is added to the revised MS. 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. Only some general discussions concerning for e.g. the impact of the pH and mineralogy on dissolution efficiency (Desboeufs et al. 2001) are added to the revised MS.

Comment 5: 32544: Size distribution of the ash: The paper focuses on the processes improving iron mobilization in the volcanic plumes to estimate its biogeochemical impact on phytoplankton, i.e. particles which can be advected and deposited from volcanic plumes to the Ocean. The size distribution of transported volcanic particles in plume (even close to the volcano) seems to be limited to 100 μm with a main fraction inferior to 20 μm (e.g. Martin et al., 2008 or Mather et al., 2004). Why do you consider particle sizes < 1mm, i.e. fine ash rather than really volcanic aerosols?

Reply: While the ash particles refer to the solid material generated through magma fragmentation inside the volcano, the particles studied by Martin et al., 2008 or Mather et al., 2004 are the liquid aerosols formed due to microphysical processes inside the

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volcanic plume and cloud. Therefore, these two kinds of particles in the eruption plume have quite different origins and physicochemical characteristics. For a detailed explanation about the fine ash size distribution please see Rose and Durant (2009). Furthermore, we focus on “plinian and sub-plinian eruption plumes” in this study while the studies mentioned by the reviewer (Martin et al. 2008; Mather et al 2004), investigate “quiescent eruption plumes”. These two plume systems are entirely different in terms of physical chemistry as well as dynamics (Sparks et al 1997). Quiescent eruption plumes have usually no ash as a major player in the system (see also Martin et al 2012, Mather et al 2003 for more details). Thus the mechanisms of aerosol formation within these two distinct systems are dissimilar. 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).

Comment 6: 32548 L9: It is interesting to know the iron dissolution from fine ash, but in a bio- geochemical context, could you provide the amount of generate soluble iron salts dependent on this dissolution, since it is this amount which will be critical to estimate the soluble iron from volcanic aerosols? Globally, it is a pity that the fraction of soluble salts is not estimated in the paper since it is really the paramount information to estimate the impact of iron ash after deposition to the ocean!

Reply: We agree with the reviewer that such estimation is scientifically very interesting. However, this could be a huge leap from talking of Fe mobilization in volcanic ash to then estimating the fraction of soluble Fe salts that may forms at ash surface through aqueous chemistry and cloud microphysics. These processes are beyond the scope of this MS. Although this estimation at global scale is not feasible in the framework of this study, we certainly keep this suggestion in mind for our future works in this filed, which

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will be focused on aqueous chemistry and cloud processing.

Comment 7: 32549 L1: The pH between 0.3 and 0.5 (Table 4) found by modeling. In order to support the reliability of your chemical results, please specify if it is an usual pH of cloud droplets in volcanic plumes?

Reply: To our knowledge, there is unfortunately no direct measurement of such pH values on volcanic ash. This is mainly because the analyzed ash samples in the literature have already undergone several other cloud processes (e.g. freezing/melting, condensation/evaporation) that significantly affect the pH but are beyond the scope of this research. Nevertheless, it is strongly suggested in several studies that the aqueous phase at the ash surface reach most likely $\text{pH} < 1$ within the first hours in the eruption plume (Ayris and Delmelle 2012, Moune et al 2009)

Comment 8: 32549 L11: Results show an impact of HCl scavenging on pH which itself control iron dissolution. Please mention that pH effect on iron dissolution from oxide is already known (e.g. Schwertmann,1991), in particular with HCl (Sidhu et al., 1981).

Reply: The suggested literature is added to the revised MS.

Comment 9: 32549 L25: “Since iron content of fayalite. . .is much higher than that of the glass, we can safely neglect the release from the glass.”. I’m not agree with that: Even if iron content in glass is low, if its solubility is very superior to the iron solubility in magnetite, the glass could be the major provider of released iron. See paper of Journet et al., 2008) which showed that illite ($\text{Fe} = 2\text{wt}\%$) is an higher provider of soluble iron than goethite ($\text{Fe} = 62\text{wt}\%$).

Reply: The reviewer is correct that glass dissolution rate is generally faster than that of minerals. But this may no longer hold at $\text{pH} < 2$ (Hamilton et al., 2000). 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

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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 (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 ash 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; Bayhurst 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 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 10: 32552 L24: the results presented in the table 5 show a large range of calculated RFe. This range is important to compare with the experimental data! So, please discuss on the parameters explaining this range (is it exclusively due to the range of Di?) in order to validate the comparison with the experimental data.

Reply: The large range in table 5 is mainly due to range of Di that is itself governed by

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two independent factors: halogen content of the gas and iron oxidation state in the ash surface. This is already mentioned in the MS but a short explanation is also added (as the reviewer suggested) to facilitate the interpretation of the reported values and their comparison with the experimental data.

Comment 11: Table 4: please precise in the legend: CP, DP, H and the cases A, B,C and D.

Reply: The legends are explained in the revised MS. The abbreviations CP, DP and HS are replaced with halogen-rich, carbon-rich and sulfur-rich gas in the revised MS, respectively.

Comment 12: Table 5: please precise the legend: CFe, Di, RFe

Reply: The legends are explained in the revised MS.

Reference:

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