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

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We appreciate the comments that helped us to improve the MS. The questions and comments are answered below.

Comment 1: The authors use proportions of Fe-bearing phases in their ash which are far in excess of realistic values. For example, in their final comparison between model output and natural ash systems, they use composition B (70% glass + 30% hematite) to derive the values in Table 5. Such a composition does not exist in any of the ash systems which the authors compare to, nor in volcanic ash generally. The authors will note that the reference cited in connection with this matter, Nakagawa and Ohba 2003, contains no mention of hematite.

Reply: We note that the values reported in table 5 are not solely based on Composition B. Indeed, the ash compositions B, C and D are combined with different gas compositions to derive these values (please see sections 4 and 5 for more details). Such a combination satisfactorily replicates all possible iron oxidation states within volcanic ash as well as the sulfur and halogen content of the gas phase leading to the Fe release ranges reported in Table 5. Therefore, focusing only on one composition in this table and neglecting the rest of the assumptions is a wrong interpretation.

As mentioned in the MS, we concentrate on processes that occur at the ash surface affecting a rim with thickness of < 100 nm (Gislason et al, 2011, Achteberg et al 2013, Hoshyaripour et al. 2014). The initial conditions also correspond to the ash surface composition at 600°C. To our knowledge, there is no published study that reports the volcanic ash surface mineralogy and composition either within this nanometer-scale rim or at temperature of 600°C. The question is how could one define a “realistic” composition for a system that has not been directly measured so far? Ash surface composition is in general known to be significantly different form its bulk composition (e.g. Delmelle et al. 2007). Thus, using the reported bulk compositions in the literature as the ash surface composition is also invalid. An alternative approach to tackle this issue is used in this MS and explained below.

Figure 1 shows a conceptual model to estimate the ash surface mineralogy and composition within the hot core of volcanic eruption plumes (T>600°C), which is governed mainly by the magma composition and the high-temperature gas-ash interactions (Hoshyaripour et al. 2014). Such processes can significantly alter the iron oxidation state at the ash surface, which also affect its solubility (Desboeufs et al 2001). Therefore, we focus on possible oxidation states of the iron: Fe2+ and Fe3+ in fayalite and hematite, respectively (as the extreme end-members). Since magnetite contains both Fe2+ and Fe3+, it is considered as an intermediate composition in the reference scenario. We assume that the behavior of these minerals (behavior here means Fe release rate) in the system is identical to that of the glass. This assumption is supported.
by several studies that reported the nearly identical dissolution behavior of identically compositioned minerals and glasses in particular under acidic conditions (see Hamilton et al., 2000 and references therein). Please see the answer to the next comment for more details about the glass dissolution.

Hematite is mainly produced in volcanic ash by oxidation and/or hydration of iron through interactions with water or ambient air during eruption (Ohba and Nakagawa 2003). Such interactions especially account for shaping the composition of the ash surface rim (considered in this study) that acts as an oxidation front during the high temperature (T>600°C) gas-ash interactions (Hoshyaripour et al. 2014). Therefore, as demonstrated through both experimental (Ohba and Nakagawa 2003) and theoretical (Hoshyaripour et al. 2014) investigations, hematite can form at the ash surface as a result of these high temperature processes.

Considering all these facts (scope of the study, data availability and the scientific backgrounds) we are convinced that the assumptions made in this study are valid and robust.

Comment 2: An additional concern is that the authors use the equations for steady-state dissolution in their calculations of proton consumption by silicate glass. As these equations are for steady-state dissolution, there is no consideration of the rapid leaching of Na, K, Ca, Mg, and to some extent Fe, that occurs during the early stages of acidic dissolution. This will likely lead to much faster consumption of protons than predicted, limiting the duration of low pH conditions at the ash surface, and presumably the extent of Fe mobilisation. In both of the above cases, the modelled systems are both chemically and mineralogically dissimilar to volcanic ash. However, the authors claim that there is good agreement between their theoretical approach and experimental measurements. If the two systems are different, the agreement of calculated values with experimental data has little scientific relevance, as the two systems cannot be causally linked. Can the authors either comment on the rationale and utility of their selected model systems, or incorporate additional data and parameters into their model to replicate more realistic ash compositions?

Reply: 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 in the comment above, i.e. the leaching of the network-modifying cations through ion exchange, is nonstoichiometric (Oelkers 2001). The question as to whether or not the stoichiometric dissolution rates could be adopted to replicate the nonstoichiometric dissolution is difficult to answer, as no published studies to our knowledge have explicitly reported such nonstoichiometric dissolution reactions and their rates at 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).

We note again that given the limited data on the initial ash surface composition, a plausible approach is to focus on not only the potential initial compositions (for e.g. concerning the iron oxidation state discussed above) but also the general behavior of the ash in the system. 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 (Ayris et al 2014, 2013). We add a new sensitivity study to the revised MS to show the similarity in the Fe release behavior of the ash in presence and absence of alkali and alkali-earth metals. For more details, please see our reply to Pierre Delmelle’s review.

Inclusion of the alkali and alkali-earth metals in the glass could be beneficial to our model but our choice is limited currently by the dissolution data availability. 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.

References:


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


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Fig. 1. Gas-ash interactions within the hot core of volcanic eruption plumes (T>600°C) (Hosh-yaripour et al 2014)