



Volcanic controls on ash iron solubility: New insights from high-temperature gas–ash interaction modeling



G. Hoshyaripour^{a,*}, M. Hort^a, B. Langmann^a, P. Delmelle^b

^a Institute of Geophysics, University of Hamburg/CEN, Bundesstr. 55, 20146 Hamburg, Germany

^b Earth and Life Institute, Université catholique de Louvain, Croix du Sud, 2 bte L7.05.10, B-1348 Louvain-la-Neuve, Belgium

ARTICLE INFO

Article history:

Received 6 May 2014

Accepted 5 September 2014

Available online 19 September 2014

Keywords:

Volcanic ash

Thermodynamic equilibrium

Iron release

Eruption plume

ABSTRACT

Recent studies strongly suggest that volcanic ash can fertilize the surface ocean by releasing soluble iron. However, the volcanic and atmospheric processes that solubilize ash iron during its transport from the volcano to the ocean are poorly understood. Using thermodynamic equilibrium calculations, we investigate the influence of gas–ash interaction within the hot core ($T > 600$ °C) of the volcanic plume and the consequences of this for ash iron solubility. Simulations are performed by considering the plume hot core as a box model in which 1000 °C magmatic gas, ash and 25 °C ambient air are mixed together. We show that mixing and the resulting cooling of the gas–ash–air mixture affect the mineralogy and oxidation state of iron in the ash surface rim. Iron mineralogy in the ash surface layer after high-temperature plume processing is primarily governed by the ratio of the H_2 and H_2S content of the magmatic gas to the amount of entrained O_2 into the hot plume (X_{mix}). The model results indicate that most of the iron in the ash surface layer is oxidized to ferric iron (Fe(III)) when $\log X_{mix}$ drops below -3.5 in the hot core. Such conditions may be encountered at convergent plate volcanoes, which release H_2O -rich magmatic gases. In contrast, high-temperature gas–ash interaction at divergent plate and hot spot volcanoes, which tend to be associated with CO_2 -rich and SO_2 -rich magmatic gases, respectively, may produce ash surfaces where iron mostly occurs as ferrous (Fe(II)). These volcanoes seem to be more favorable for iron fertilization because $\log X_{mix}$ does not fall below -3.5 and $>80\%$ of the iron in the ash surface remains ferrous (Fe(II)), which is more soluble in water than Fe(III).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

After the 1991 eruption of Mt. Pinatubo, Philippines, it was hypothesized that ash in contact with seawater releases iron and other nutrients in sufficient amounts to the surface ocean to stimulate marine primary productivity (MPP) and in turn, global atmospheric CO_2 draw-down (Sarmiento, 1993; Watson, 1997). Frogner et al. (2001) found that the ash from the eruption of Hekla in 2000, Iceland, released significant amounts of dissolved iron, silicon, and manganese together with sulfate, chloride and fluoride upon exposure to seawater. Subsequent studies have confirmed that volcanic ash affects MPP through rapid soluble iron release upon contact with seawater (Duggen et al., 2007). The first direct evidence of a phytoplankton bloom following fertilization by volcanic ash deposition was reported by Langmann et al. (2010) and later, Hamme et al. (2010) in the wake of the 2008 eruption of Kasatochi volcano in the Aleutian Islands. Achterberg et al. (2013) also reported a significant perturbation in the biogeochemistry of the Iceland Basin of the North Atlantic through the dissolved iron release from the ash erupted from Eyjafjallajökull, Iceland, in 2010.

Volcanic ash refers to tephra with a diameter of <2 mm (Rose and Durant, 2009) and is typically composed of silicate glass and crystalline materials generated during an explosive eruption through magma fragmentation and to some extent, through erosion of the conduit wall rock (Heiken and Wohletz, 1992). Iron in volcanic ash produced through magma fragmentation is essentially found 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). However, the source of bio-available iron involved in the alteration of the surface ocean's biogeochemistry is believed to be soluble iron species on the ash surface (Duggen et al., 2010; Hamme et al., 2010; Achterberg et al., 2013). Bio-availability of iron is suggested to be strongly linked to its solubility, which is influenced by chemical speciation (Fe(II) is more soluble), mineralogy (amorphous phases are more soluble), and Al substitution in Fe(III) oxides (Al-rich Fe phases are less soluble) (von der Heyden et al., 2012). Volcanic and atmospheric processes that modulate these properties and consequently, ash iron solubility are poorly constrained so far. Ayris and Delmelle (2012) emphasized that both high and low temperature reactions within the eruption plume can significantly alter the ash surface composition, and hence iron mineralogy and speciation. These reactions are expected to modify the surface reactivity of the ash, thus potentially influencing further (photo)chemical reactions during transport of the ash in the atmosphere.

* Corresponding author. Tel.: +49 40 42838 5053.

E-mail address: gholamali.hoshyaripour@zmaw.de (G. Hoshyaripour).

Within the hot core of the eruption plume (named as the effective source region in earlier studies; Martin et al., 2006; Roberts et al., 2009), where temperatures above 600 °C prevail, scavenging of magmatic volatiles (SO₂, HCl and HF) can take place through gas–ash interaction (Rose, 1977; Óskarsson, 1980; Ayris et al., 2013). The reactions between these gases and the ash surface are thought to be partly responsible for the deposition of alkali and alkaline-earth sulfate and chloride salts on the ash surface (Delmelle et al., 2007). Recent modeling studies show that admixture of air with magmatic gases in the hot core of a volcanic eruption plume leads to a wide range of reactions and significant alteration of the gas composition (Gerlach, 2004; Martin et al., 2006, 2009; Bobrowski et al., 2007; Roberts et al., 2009). In the hot core ($T > 600$ °C), the reaction rates are sufficiently fast to ensure that the system is close to thermodynamic equilibrium conditions (Symonds and Reed, 1993).

Here we investigate gas–ash interaction in the hot core of the volcanic plume in order to explore the effect of this zone of the plume on iron mineralogy and oxidation state in the ash's surface. The model framework and assumptions are presented in Section 2. High temperature (here after referred to as high-T) gas–ash interaction is then simulated for three distinct volcanic gas compositions to represent the geochemical patterns of main volcano-tectonic settings. A sensitivity analysis with respect to initial conditions (e.g., magma oxidation state, ash composition, etc.) is performed in Section 3. Finally, the influence of ash processing within the hot core on the redox state of iron in ash is discussed in Section 3. We hasten to emphasize that this study does not intend to reproduce any data or specific situation at one volcano but to explore the role of high-T volcanic gas–ash interaction in iron speciation and mineralogy in different tectonic settings in general.

2. Methodology

2.1. Conceptual model

We consider the hot core of sub-plinian and plinian eruption plumes as a box model which covers the chemical processes in the temperature range 1000 °C $>$ $T >$ 600 °C (Fig. 1). Assuming thermodynamic

equilibrium in this zone of the plume, we use GASWORKS (Symonds and Reed, 1993), to simulate the interaction among magmatic gases, ash and atmospheric gases. GASWORKS computes heterogeneous equilibria among gases, solids and liquids during the processes of cooling, gas–gas mixing, pressure changes and gas–rock reactions. For more details about GASWORKS we refer the readers to Symonds and Reed (1993). In this study we assume that only surface layer of the ash (the 1–100 nm thick rim shown in Fig. 1) interacts with the surrounding gases according to thermodynamic equilibrium (kinetics is negligible). The theory and calculations behind this assumption are explained in details in Appendix A.

2.2. Gas and ash mixture

Olgun et al. (2011) observed that ash from different volcanic settings release different amounts of iron upon contact with seawater. Therefore, we use the high-T gas composition corresponding to the three main volcanic settings (convergent plate (CP) or H₂O-rich, divergent plate (DP) or CO₂-rich and hot spots (HS) or SO₂-rich) (Table 1). Although these average compositions do not rigorously cover all the observed high-T magmatic gases, they satisfactorily represent the geochemical differences between tectonic settings (e.g., water, sulfur, carbon and halogen contents; Symonds et al., 1994).

The solid mass associated to particle sizes < 64 μm is considered in this study, which may represent a substantial contribution ($> 50\%$) to tephra deposits from explosive volcanic eruptions (Rose and Durant, 2009). Particles in this size range not only have more specific surface area for interaction with the gas phase (Delmelle et al., 2005) but also can be lifted to high altitudes (Sparks et al., 1997). In order to determine the initial ash bulk composition, we use the method recommended by Symonds and Reed (1993) where magma of a given composition (for the whole rock composition used here see Table 2) is titrated into the gas phase step by step until a certain gas/rock ratio is reached. GASWORKS then determines the composition of minerals being in equilibrium with the given gas composition at a prescribed temperature, oxygen fugacity (f_{O_2}) and pressure ($P = 1$ atm).

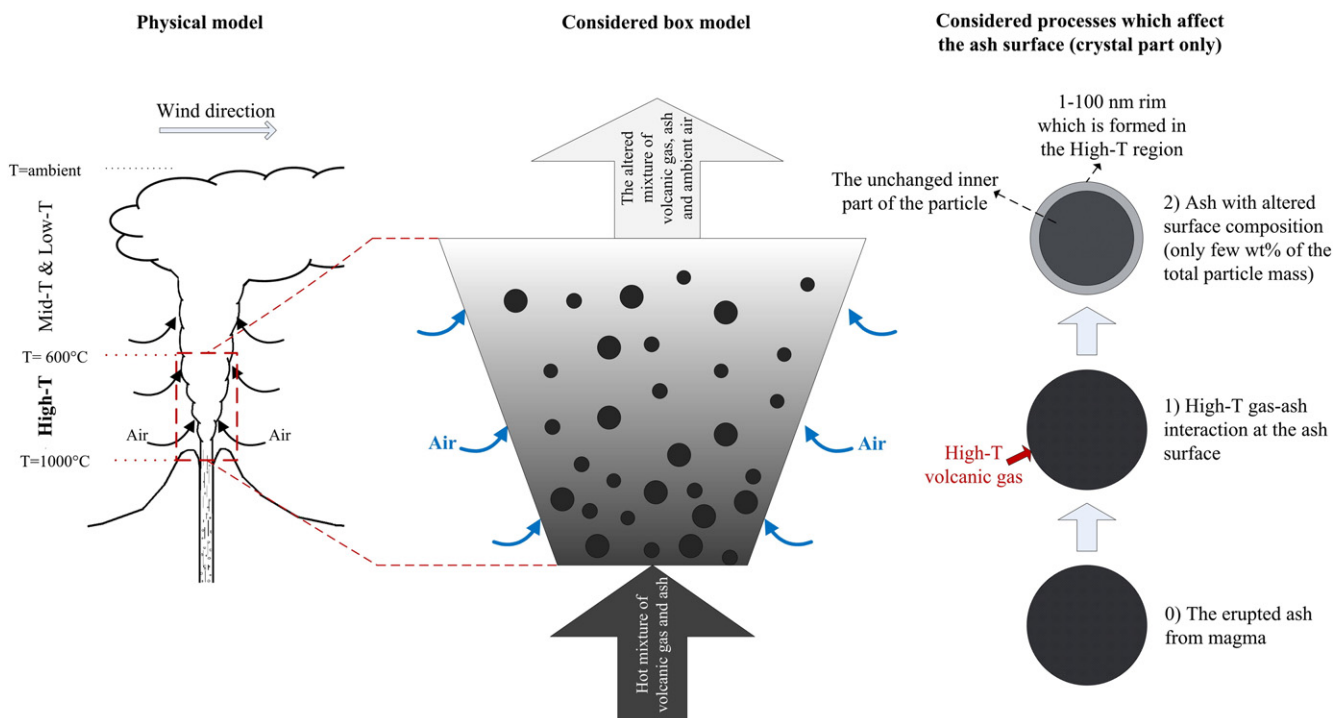


Fig. 1. Sketch of the box model used for simulating gas–ash interaction within the volcanic plume hot core.

Download English Version:

<https://daneshyari.com/en/article/6439657>

Download Persian Version:

<https://daneshyari.com/article/6439657>

[Daneshyari.com](https://daneshyari.com)