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Reaction Rates Control High-Temperature Chemistry of Volcanic Gases in Air

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When volcanic gases enter the atmosphere, they encounter a drastically different chemical and physical environment, triggering a range of rapid processes including photochemistry, oxidation, and aerosol formation. These processes are critical to understanding the reactivity and evolution of volcanic emissions in the atmosphere yet are typically challenging to observe directly due to the nature of volcanic activity. Inferences are instead drawn largely from observations of volcanic plumes as they drift across a crater's edge and further downwind, and the application of thermodynamic models that neglect reaction kinetics as gas and air mix and thermally equilibrate. Here, we foreground chemical kinetics in simulating this critical zone. Volcanic gases are injected into a chain-of-reactors model that simulates time-resolved high-temperature chemistry in the dispersing plume. Boundary conditions of decreasing temperature and increasing proportion of air interacting with volcanic gases are specified with time according to an offline plume dynamics model. In contrast to equilibrium calculations, our chemical kinetics model predicts that CO is only partially oxidized, consistent with observed CO in volcanic plumes downwind from source. Formation of sulfate precursor SO_3 at $SO_3/SO_2 = 10^{-3}$ mol/mol is consistent with the range of reported sulfate aerosol to SO_2 ratios observed close to crater rims. High temperature chemistry also forms oxidants OH, HO_2, and H_2O_2. The H_2O_2 will likely augment volcanic sulfate yields by reacting with $SO_{2(aq)}$ in the cooled-condensed plume. Calculations show that high-temperature OH will react with volcanic halogen halides (HBr and HCl) to yield reactive halogens (Br and Cl) in the young plume. Strikingly, high-temperature production of radical oxidants (including HO_x) is enhanced by volcanic emissions of reduced gases (CO, H_2, and H_2S) due to chemical feedback mechanisms, although the kinetics of some reactions are uncertain, especially regarding sulfur. Our findings argue strongly that the chemistry of the hot near-source plume cannot be captured by equilibrium model assumptions, and highlight the need for development of more sophisticated, kinetics-based, high-temperature CHONS-halogen reaction models.

Keywords: thermodynamic equilibrium model HSC, combustion kinetics model chemkin, high-temperature, magmatic gas emission, at-source primary sulfate, volcano plume, volcanic eruption, sulfuric acid

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INTRODUCTION

Volcanoes release gases and aerosols to the atmosphere through both quiescent (passive) degassing, and effusive and explosive eruptions. Volcanic emissions of SO_2 to the stratosphere are well known to impact climate through the atmospheric oxidation of SO_2 to form radiatively active sulfate aerosol particles. In fact, volcanoes release a wide range of highly reactive gases that can impact atmospheric composition and climate. Volcanic bromine and chlorine emissions undergo plume atmospheric chemistry that can destroy both tropospheric and stratospheric ozone. In descending order of typical abundance (which varies with volcano setting, magma redox conditions, and eruptive style) volcanic gas emissions consist of: H_2O, CO_2, SO_2, HCl, HF, H_2S, OCS, CO, and HBr, as well as other trace species e.g., metals. Observations of volcanic plumes identify several additional species (e.g., NO, NO_2, HNO_3, BrO, OClO, SO_4^{2-}, HO_2NO_2, and H_2O_2), (Allen et al., 2000; Mather et al., 2004b; Bobrowski et al., 2007; Oppenheimer et al., 2010; Carn et al., 2011; Martin et al., 2012; Kern and Lyons, 2018). These species are formed by oxidizing chemical reactions as the magmatic gases mix with air, first at high temperatures near to the source and then at low temperatures as the cooled plume disperses further into the background atmosphere. Numerical models of low-temperature atmospheric chemistry of the plume have been developed (e.g., Bobrowski et al., 2007; Roberts et al., 2009; von Glasow, 2010; Jourdain et al., 2016) that are able to reproduce some – but not all – of these observed oxidized species. This points to an important role of high-temperature chemistry. Current approaches apply thermodynamic equilibrium models to represent the high-temperature chemistry of the near-source plume (e.g., Gerlach, 2004; Martin et al., 2006). However, thermodynamic equilibrium calculations may be misleading if the chemistry is limited by kinetics (rates of reactions) in the rapidly cooling volcanic gas and air mixture within seconds of emission. Here, a chemical kinetics approach is developed to simulate the time-varying chemical processing of C-H-O-S gases in the hot near-source plume on its release and mixing with background air.

High-Temperature Products in Volcanic Plumes: Observations and Modeling

Observational evidence for the high-temperature production of oxidants in volcanic plumes includes SO_{xy}, HO_{xy}, NO_{xy}, and rapid formation of reactive halogens. Sulfate-rich aerosols have been observed at the crater-rim or in very near-downwind plumes of many volcanoes (exception: volcanic domes), **Table 1**. Sulfate is reported relative to co-measured SO_2 which serves as a convenient yet only approximate plume tracer, allowing observations to be normalized for dilution effects. The sulfate:SO_2 ratios typically range from 0.00002 up to around 0.01 mol/mol, **Table 1** and references therein. Many of the ratios are too high to be explained by atmospheric oxidation of SO_2 at low-temperatures on the plume transport timescale of seconds to minutes (e.g., Galeazzo et al., 2018). Instead, the observations indicate a sulfate-rich aerosol formed very close to source. One hypothesized pathway to its formation is high-temperature oxidation of a small fraction of SO_2 in the near-source plume to produce sulfate precursor SO_3 (Allen et al., 2000). For volcanic domes, sulfate formation may be enhanced by circulation of air inside the dome (Zelenski et al., 2015). The range in observed SO_4^{2-}:SO_2 indicates variability in the near-source sulfate formation processes at different volcanoes, as well as possibly some measurement uncertainty. In all cases sulfate contributes a minor fraction to the total sulfur emission that is typically dominated by SO_2 and H_2S (the proportion depending strongly on magma redox conditions; Oppenheimer et al., 2014). Nevertheless, at source (or so-called "primary") volcanic sulfate is critical to plume processes such as multi-phase halogen reactions (discussed further below) and acts as a condensational sink that can inhibit new particle formation (Sahyoun et al., 2019).

There exist few measurements of volcanic HO_{xy}. Carn et al. (2011) report in-cloud processing of SO_2 from the Huila volcanic plume by H_2O_2, with plume H_2O_2 abundance elevated above background by about 0.5 ppbv. This volcanic H_2O_2 might have

TABLE 1 | Observational evidence for at-source sulfate aerosol in volcanic plumes.

Volcano	SO_4^{2-}/SO_2 mol/mol	References
Kilauea	0.005 0.077, 0.016, and 0.001	Naughton et al., 1975; Kroll et al., 2015
Erta Ale	0.005, 0.008, 0.006, 0.007, 0.001, 0.007, and 0.006	de Moor et al., 2013
Lascar	0.01	Mather et al., 2004b
Masaya	0.0006–0.007, average: 0.0015 (0.0008–0.0105 mass ratio)	Allen et al., 2002
	0.006, 0.006, 0.01, and 0.013	Mather et al., 2003
	0.0055, 0.0053, 0.0064, 0.0108, 0.0052, 0.0074, 0.0493, 0.0003, 0.0058, 0.0052, 0.0046, and 0.0684 (0.0053 regression)	Martin et al., 2010
	0.023, 0.036	de Moor et al., 2013
Etna	0.017, 0.049, and 0.05 0.01–0.02	Martin et al., 2008; Roberts et al., 2018
Villarrica	0.02	Mather et al., 2004b
Redoubt (1990 eruptions)	0.001	Hobbs et al., 1991
Montserrat (crater-edge) Montserrat (dome)	0.03 (0.04 mass ratio) 0.5 (0.7 mass ratio)	Allen et al., 2000
Bezymianny (dome)	0.43	Zelenski et al. (2015)
Eyjafjallajökull 2010 fire-fountaining Eyjafjallajökull 2010 cooling lava flow	0.00002, 0.0014, and 0.0044 0.063	Ilyinskaya et al., 2012

Lascar and Monsterrat mass ratios were converted into molar ratios assuming masses of SO_4 and SO_2.

originated from the self-reaction of volcanic HO_2. Oppenheimer et al. (2010) measured elevated HO_2NO_2 in the (cooled and dilute) Mt Erebus plume where the cold Antarctic atmosphere likely contributed to its thermal stability. HO_2NO_2 is formed by the reaction of HO_2 with NO_2 therefore its presence provides evidence for volcanogenic sources of both HO_x and NO_x. Volcanogenic HO_x has also been observed by a chance encounter of an instrumented aircraft with the Hekla 2000 eruption plume in the lower stratosphere (Rose et al., 2006). Observations showed OH and HO_2 were elevated at up to 0.5 and 15 pptv above background in 33–34 h aged volcanic cloud during night. These measurements have eluded any explanation given the lack of photochemistry, a cooled plume, and anticipated fast HO_x destruction by reaction with volcanic SO_2 and halogens (both in excess abundances). In general, the reported elevated abundances of HO_{xy} in volcanic plumes compared to the background atmosphere are surprising because low-temperature volcanic plume chemistry is expected to deplete HO_{xy} (Galeazzo et al., 2018). Volcanic HO_{xy} may originate from high-temperature chemistry of the near-source plume.

Elevated concentrations of NO, NO_2, and HNO_3 have been measured in several volcanic plumes in the troposphere in addition to the HO_2NO_2 observed in the Mt Erebus plume: a review is given by Martin et al. (2012) and references therein, reporting a typical molar ratio for NO_y/H_2O of 10^{-5}. Whilst filter pack sampling identified HNO_3 in crater-rim plumes from several volcanoes (e.g., Mather et al., 2004a), on other occasions there was no evidence for HNO_3, even at the same volcano (e.g., Martin et al., 2010). This may point to variability in emissions-processing or reliability of measurement technique. Nevertheless, real-time aircraft-based measurements by Atmospheric Chemical Ionization Mass Spectrometer confirm volcanic HNO_3 in plumes downwind from Mt Etna at HNO_3/SO_2 = 0.02 (Voigt et al., 2014), and in the Mt Erebus plume (Oppenheimer et al., 2010). Sources of volcanic NO_{xy} are uncertain. Martin et al. (2012) present a kinetic model of CHON chemistry that demonstrates high-temperature formation of thermal NO_x is too slow to occur in the near-source plume that rapidly disperses and cools over seconds-minutes. Volcanic lightning is a likely source of NO_x in clouds from explosive eruptions. It has also been hypothesized that NO_x may sometimes be formed by oxidation of ammonia, for example in the stratospheric cloud from the Hekla 2000 eruption (Rose et al., 2006).

The need to characterize high-temperature chemistry in the near-source plume is underlined by model studies of volcanic halogen transformations in the plume (Bobrowski et al., 2007; von Glasow, 2010; Roberts et al., 2014). Halogens are emitted as hydrogen halides (HBr and HCl) from volcanoes but are transformed into reactive halogens (BrO and OClO) in the tropospheric plume via a multi-phase autocatalytic "bromine-explosion" chemistry occurring at low-temperatures. However, numerical models of the plume atmospheric halogen chemistry can only reproduce the observed magnitude and rate of formation of BrO if the volcanic emission is modified to include radicals believed to form at high-temperatures in the near-source plume (the so-called "effective source region"). Radicals such as OH (that react with HBr, HCl to produce Br, and Cl) provide an initial source of reactive bromine to initiate the low-temperature bromine explosion cycles. Furthermore, high-temperature production of sulfate-precursor SO_3 generates near-source (so-called "primary") sulfate aerosols that promote heterogeneous reactions that drive the bromine explosion chemistry. Observations of BrO (and occasionally OClO) in tropospheric volcanic plumes globally (e.g., Bobrowski et al., 2007; Boichu et al., 2011; Hörmann et al., 2013; Donovan et al., 2014; Kern and Lyons, 2018) indicate pervasive emissions of volcanic halogens to the troposphere accompanied by both high- and low-temperature chemistry in volcanic plumes.

The high-temperature region of the plume also facilitates gas-ash interactions including adsorption of gases such as SO_2 and HCl onto ash particles that may then fall-out (Delmelle et al., 2018 and references therein). High-temperature SO_3 is a precursor to sulfate that can condense as the eruption column cools and could change ash properties (e.g., Hoshyaripour et al., 2015) and ash-related atmospheric impacts e.g., regarding plume lightning or ice nuclei. Whilst such heterogeneous interactions are outside the scope of our study, quantifying the high-temperature oxidizing chemistry occurring in the gas-phase as volcanic gases mix with air is a fundamental first-step to characterising the near-source plume composition and its possible influence on gas-ash interactions.

Thermodynamic models such as HSC have been applied to calculate the equilibrium compositions of mixtures of magmatic gases with air, and HSC output has been used in numerical model studies of the plume atmospheric chemistry and impacts (e.g., Gerlach, 2004; Martin et al., 2006, 2007, 2009, 2011; Aiuppa et al., 2007; Bobrowski et al., 2007, 2015; Roberts et al., 2009, 2014, 2018; von Glasow, 2010; Martin and Ilyinskaya, 2011; Hoshyaripour et al., 2012; Ilyinskaya et al., 2012; Surl et al., 2015; Jourdain et al., 2016). HSC is used to calculate the composition of the near-source plume for temperatures above 600°C according to Gibbs free energy minimization. The emission is released at magmatic temperatures and as the magmatic gases entrain air, the mixture cools toward background temperature. The calculation assumes thermodynamic equilibrium composition is reached at a specified temperature and degree of mixing of air with magmatic gases (often expressed as a volumetric or molar ratio, VA:VM where VA is air volume and VM is magmatic gas volume). Plume composition is then assumed to be "quenched" with respect to high-temperature chemistry upon further mixing with air. Choice of the VA:VM "quenching-point" for the HSC calculation is rather uncertain and may vary with eruption/emission type. For studies of passively degassing volcanoes it was found that a high VA:VM = 40:60 (Bobrowski et al., 2007) yielded extremely high SO_3 relative to SO_2 (much greater than observed sulfate/SO_2 ratios, see **Table 1**), therefore more recent studies chose lower VA:VM = 10:90 or 5:95 (e.g., Roberts et al., 2014) as the point where high-temperature chemistry is quenched. Conceivably, large eruptions might sustain high-temperature conditions over longer periods allowing the chemistry to reach equilibrium conditions at higher VA:VM. Hoshyaripour et al. (2012) simulated the high-temperature chemistry in an eruption column by co-varying VA:VM from 0 to 1 with temperature decreasing

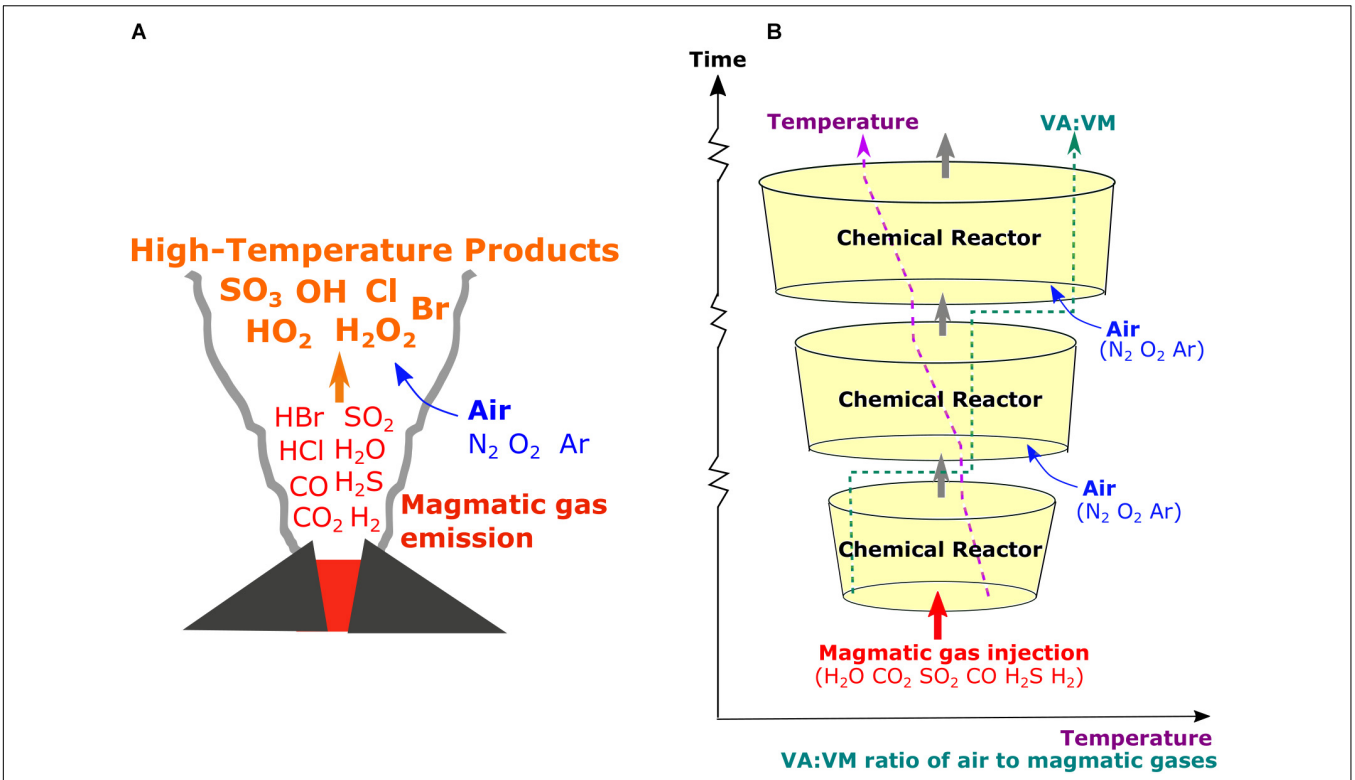

FIGURE 1 | Schematics of **(A)** high-temperature plume chemistry that generates radicals and oxidized products in the plume and **(B)** our chain-of-reactors approach to simulate the processes based on chemical kinetics under time-varying temperature (T) and proportion of mixing of air with magmatic gases (VA:VM).

from 1273 K to 873 K (1000°C to 600°C), predicting that the eruption column acts as a hot oxidizing reactor for S species.

In general, volcanic plume applications of thermodynamic equilibrium models such as HSC yield elevated abundances of SO_x (dominated by SO_3), HO_x (dominated by OH) and NO_x (dominated by NO), and halogen radicals Br, Cl (e.g., Martin et al., 2006). The relative abundances of these oxidized products increase with increasing VA:VM. The equilibrium models also predict near-complete oxidation of reduced gases emitted from volcanoes (e.g., CO, H_2S, and H_2), yet these gas species are often detected at the crater-rim or in downwind (cooled) plumes (e.g., Aiuppa et al., 2005; Schumann et al., 2011; Moussallam et al., 2012; Roberts et al., 2012; de Moor et al., 2016). This suggests that some gas species may not always be under equilibrium control (Martin et al., 2009). Plume observations of reduced gases relative to major gases (e.g., CO/CO_2, H_2/H_2O, and H_2S/SO_2) are used to infer emission properties such as temperature and oxidative state, but such inferences cannot hold true if there is substantial oxidation of the reduced gases following emission, as predicted by HSC. Here, a method is developed to evaluate how reaction rates control high-temperature chemistry of volcanic gases in air as a function of time-varying plume dynamics, **Figure 1**.

Our model uses a chemical kinetics rather than thermodynamics approach, and requires time-resolved boundary conditions in both temperature and degree of mixing of magmatic gases with air (VA:VM), as well as the composition of the volcanic gases emitted as model input. The temperature of the volcanic gas emission is uncertain. It is typically assumed to be identical to petrological magmatic estimates (600–1200°C), although analysis of gas compositions measured at Kilauea, Hawaii (Oppenheimer et al., 2018) and Mt Etna, Italy (Aiuppa et al., 2011) show that gases may cool prior to emission into the atmosphere. Introduction of surface waters may also cool the gas emission. Physical properties of the plume are poorly constrained for the few seconds following release from the eruptive vent (or other emission sources e.g., lava lake or dome), as there are few direct measurements or dedicated model studies. A study of gas-puffing dynamics at passively degassing volcano Masaya yielded estimates of mean dilutions of 0.09 and 0.24 between emission and detection by thermal radiometer about 5–10 m above the vent, for gas puffs with mean velocities 2.5 and 4.3 m/s (Branan et al., 2008).

One way to estimate temperature and VA:VM in the near-source plume can be through dynamical model simulations of plume rise (e.g., Mastin, 2007; Aubry et al., 2017). This study relies on one such eruptive case to supply physical boundary conditions: the PlumeRise model applied to the 2010 Eyjafjallajökull eruption plume (Woodhouse et al., 2013), for which observations of volcanic gases including CO/SO_2 have also been reported both close to the source and far downwind (Allard et al., 2011; Schumann et al., 2011). This Eyjafjallajökull case forms the basis for an exploratory investigation into the chemical kinetics of gas-phase reactions occurring at high-temperatures in volcanic plumes.

MATERIALS AND METHODS

Our approach to simulate high-temperature chemical reactions in the near-source plume includes three components: (i) the chemical kinetics model (chain-of-reactors), (ii) physical boundary conditions applied to the model, and (iii) the volcanic gas emissions injection as model input.

Chemical Kinetic Model (Chain-of-Reactors)

Chemkin is a fortran-based tool for incorporating complex chemical kinetics into model simulations of fluid dynamics (Kee et al., 2000 and related references from Reaction Design). Gas species and (reversible) reactions are first declared, as well as initial conditions (such as initial gas concentrations, temperature, pressure), and then the reactions are simulated in a plug-flow reactor (PFR) to evaluate temporal changes in gas composition.

Rates of progressions of reactions are quantified as the difference between the rate of the forward and reverse reactions, for example E1 for the reversible reaction A + B = C + D (where gases A, B, C, and D may also be involved in other reactions, each with its corresponding differential equation).

$$\text{E1} \quad d[C]/dt = k_f \times [A] \times [B] - k_r \times [C] \times [D]$$

The rate constants for forward reactions, k_f, are described in the form, E2, where R is the gas constant and T the gas temperature. The pre-exponential factor, A, the temperature exponent, β, and activation energy E, are specified in the mechanism file (see Glarborg and Marshall, 2013).

$$\text{E2} \quad k_f = A \times T^{\beta} \times \exp[-E/(R \times T)]$$

The reverse reaction rate constant, k_r, is given by E3 where K is the equilibrium constant that is determined by thermodynamic properties (molar enthalpies and entropies as a function of temperature); these properties are specified in the thermodynamic data file (see Glarborg and Marshall, 2013).

$$\text{E3} \quad k_r = k_f/K$$

The Chemkin model also accounts for third-body, unimolecular, chemically activated reactions, and pressure-dependencies of reaction rates. The resulting system of ordinary differential equations and initial conditions is solved by Chemkin to quantitatively predict how the gas composition in the chemical reactor evolves as a function of time according to the kinetics-based reaction scheme and the thermodynamic conditions.

The reaction mechanism applied within ChemKin is user-specified. There are very few studies at high-temperature dealing with sulfur species oxidation and their interactions with carbon, nitrogen oxides, or halogens. Here, the mechanism proposed by Glarborg and Marshall (2013) was selected for its good performance in comparison to laboratory shock-tube experiments, as recently highlighted by Mathieu et al. (2017). It includes 38 species involved in 161 reversible reactions. This reaction mechanism, and corresponding thermodynamic properties, relies on earlier works on sulfur chemistry and was updated to model the oxidation of carbonyl sulfide (OCS). A full list of gas species and chemical reactions is given in **Supplementary Tables S1**, **S2**. This version does not include halogens or NO_x chemistry. The interactions between sulfur, carbon, halogens, and nitrogen oxides are beyond the scope of this work, but will need to be addressed in future. Also, all the species considered were in the gas-phase; heterogeneous reactions or photochemical reactions were not included. This is a clear limitation of the present study which should be seen as a preliminary step needed to account for time evolution of chemicals in a near-source plume. Whilst the chemical scheme is one of the most complete regarding sulfur compounds, there exist some uncertainties in the high-temperature reaction kinetics, in particular related to H_2S (Mathieu et al., 2017). A single PFR simulates the high-temperature chemistry for given starting conditions in gas composition and temperature. A time-varying temperature can be introduced by applying a temperature gradient in the PFR and imposing an initial velocity of the reactor gases. However, air cannot be added as a function of time into a single reactor, i.e., the proportion of air to magmatic gases in the simulation is held constant according to the initial composition.

Therefore, a chain-of-reactors approach was developed using the Chemkin Pro software to simulate the chemical evolution of a near-source plume that simultaneously cools (decreasing T) and entrains air (increasing VA:VM) as it dilutes, **Figure 1**. Thirty PFRs were placed in a chain. A continuous decreasing trend in plume temperature was imposed across the chain by defining the start and end temperatures for each PFR according to our chosen boundary conditions (details in the next section). The starting composition for each reactor was defined by taking the output from the preceding one and diluting it with air (78% N_2, 21% O_2, 1% Ar) according to time-varying VA:VM boundary conditions. The pressure decrease was also considered even if it was not found to be significant. This alternate simulation of the plume chemistry (within reactor boxes) and mixing-dilution steps (between reactor boxes) is similar to the approach used in kinetics-based modeling of the low-temperature atmospheric chemistry of volcanic plumes e.g., PlumeChem (Roberts et al., 2009).

Boundary Conditions to the Chain-of-Reactors Provided by PlumeRise Model

The chain-of-reactors model requires time-resolved boundary conditions for plume temperature and VA:VM as the emitted volcanic gases rapidly mix with air. Here, output from the 1D PlumeRise model is used. PlumeRise describes the ascent of a turbulent buoyant plume composed of solid pyroclasts, magmatic gases, and air and includes the effects of cross-wind on turbulent entrainment of air into the plume. The PlumeRise dynamics model approximates volcanic gases as entirely H_2O (a more complex emission composition provides input to the chain-of-reactors model, see Section "Magmatic Gas Emissions" below).

Output from the PlumeRise model includes the plume temperature (T, in K), the total mass flux (Q in kg/s), the gas

mass fraction (n), the vertical velocity, U (m/s), the mass fraction of water (liquid+gas) in the plume (φ), specific humidity (C), and altitude (z in m), each provided at a resolution (dz) of a few meters. These variables can be used to derive temperature and VA:VM as a function of time. The time, in seconds is given by E4, and integrating dt.

$$\text{E4} \quad dt = dz/U$$

The plume total mass (gases and solids), M in kg, in the discrete volume at each time-step is given by E5.

$$\text{E5} \quad M = dz \times Q/U$$

The mass of all gases (volcanic H_2O and air) in the plume, $M_{(g)}$ is the product of M and the gas mass fraction, n, E6.

$$\text{E6} \quad M_{(g)} = n \times M$$

Under high temperature plume conditions, all H_2O in the plume is in gaseous form, whose mass $M_{(w)}$ is the product of M and φ, E7.

$$\text{E7} \quad M_{(w)} = M \times \varphi$$

The mass of dry air in the plume, $M_{(da)}$ is the difference between $M_{(g)}$ and $M_{(w)}$, E8. The mass of background water in the plume, $M_{(bw)}$ is the product of $M_{(da)}$ with the specific humidity, C, E9. The mass of volcanic gases (here: entirely as H_2O), $M_{(vg)}$, is the difference between $M_{(w)}$ and $M_{(bw)}$, E10.

$$\text{E8} \quad M_{(da)} = M_{(g)} - M_{(w)}$$

$$\text{E9} \quad M_{(bw)} = M_{(da)} \times C$$

$$\text{E10} \quad M_{(vg)} = M_{(w)} - M_{(bw)}$$

The masses $M_{(vg)}$, $M_{(da)}$, and $M_{(bw)}$ in kg are converted into moles of volcanic gases, dry air, and background water, $m_{(vg)}$, $m_{(da)}$, $m_{(bw)}$, by dividing by their respective molecular weights (18×10^{-3} for H_2O and 29×10^{-3} for dry air containing N_2, O_2, and Ar, expressed as kg/mol), E11,12,13. The total moles of entrained wet air, $m_{(air)}$, is calculated by the sum of $m_{(da)}$ and $m_{(bw)}$, E14.

$$\text{E11} \quad m_{(da)} = M_{(da)}/(29 \times 10^{-3})$$

$$\text{E12} \quad m_{(vg)} = M_{(vg)}/(18 \times 10^{-3})$$

$$\text{E13} \quad m_{(bw)} = M_{(bw)}/(18 \times 10^{-3})$$

$$\text{E14} \quad m_{(air)} = m_{(da)} + m_{(bw)}$$

Finally, the ratio VA:VM is the moles of wet air divided by moles of volcanic gases, E15.

$$\text{E15} \quad VA : VM = m_{(air)}/m_{(vg)}$$

The calculation yields VA:VM as a function of dz or time when performed for each row of output from the 1D plume dynamics model. Assumptions that water exists purely in the gas phase and that water content is dominated by the volcanic emission are valid for the hot and concentrated plume region investigated in this study. The resulting trend in temperature with VA:VM is consistent with simple specific-heat calculations for the magmatic-air-ash mixture. Plume temperature and VA:VM depend strongly on the T, n, U starting conditions used for the PlumeRise model.

Several PlumeRise 1D model results showing decreasing temperature and increasing VA:VM with time or distance from the source are shown in **Supplementary Figure S1**, for the Eyjafjallajökull eruption April 14–17, 2010. These are based on the model runs of Woodhouse et al. (2013) that used meteorological data from local balloon soundings[1]. The model input parameters are only partially constrained, but Woodhouse et al. (2013) found good predictive capability of the model to reproduce plume height for starting parameter ranges of temperature T = 600–1000 K, vertical velocity U = 50–100 m/s, gas mass fraction n = 0.030–0.086 (Woodhouse et al., 2013; **Supplementary Table S3**). Notably, the model runs are highly diverse in their starting temperatures and predicted VA:VM. The starting temperatures are all substantially lower than petrological estimates of the magmatic temperature, (Keiding and Sigmarsson, 2012) who reported 1443 K (1170 ± 25°C) for the early flank eruption, and 1273–1333 K (1000-1060°C) for benmoritic products related to the main summit eruption that are pertinent to this study. Reasons for this are unclear but could be due to decoupling of magmatic and gas temperatures or a cooling effect of incorporated water. The Introduction Section "High-Temperature Products in Volcanic Plumes: Observations and Modeling" highlighted considerable uncertainty in the physical conditions (temperature, VA:VM) of the near-source plume.

In this exploratory study we use output from the PlumeRise simulation with starting temperature at 1000 K as example boundary conditions in time-varying T and VA:VM as a basis for chemical kinetics modeling of the hot plume chemistry. This chosen PlumeRise dynamics scenario from Woodhouse et al. (2013) combined with magmatic gas emissions based on Allard et al. (2011; **Table 2**) yields an SO_2 flux of 5.5 kt/hr SO_2, that is consistent with the range of SO_2 fluxes derived from satellite observations during the Eyjafjallajökull eruption (Boichu et al., 2013).

Magmatic Gas Emissions

A volcanic gas emission composition is input to the chain-of-reactors model, based on reported observations. It should be emphasized that available observations are an imperfect basis for the initialization of model of high-temperature chemistry in the near-source plume. First, no individual measurement technique can observe all gases in a volcanic plume. Available observations may not fully characterize all magmatic gases in the emission, nor any temporal evolution in their release as a function of volcanic activity. Second, observations of the cooled or partially cooled plume necessarily already incorporate any high-temperature modification of the emissions. Our use of such observations inherently assumes that preceding plume chemistry has only slightly modified the volcanic gas emission. This is indeed the prevalent assumption behind near-source monitoring

[1]http://weather.uwyo.edu/upperair/sounding.html

TABLE 2 | Magmatic gas compositions (mole fraction) used as input to the chain-of-reactors model simulations.

Volcanic gas	Eyja CO	Eyja CO-H_2S-H_2
H_2O	0.916	0.916
CO_2	0.08	0.08
SO_2	0.002	0.002
H_2S	–	0.00000145
HCl	X (0.0013)	X (0.0013)
HF	–	–
HBr	–	–
H_2	–	0.00237
CO	0.00035	0.00035

X means that the gas was replaced by Ar. The emission composition is based on field-observations of Eyjafjallajökull's summit 2010 eruption (Allard et al., 2011). A second Eyjafjallajökull emission scenario includes theoretical estimates of H_2 and H_2S. A sensitivity study also investigated emissions excluding CO or SO_2.

of volcanic gas emissions (with the exception of volcanic BrO, e.g., Guttmann et al., 2018). Unfortunately, sources such as lava bodies are typically hazardous and inaccessible, therefore few direct measurements are available of the gas emission prior to any mixing with air.

In this study the composition of the Eyjafjallajökull magmatic gas emission is based on observations of H_2O-CO_2-SO_2-CO-(HCl) in the young plume of the summit eruption reported by Allard et al. (2011) who performed FTIR spectroscopy of volcanic gases in early May 2010, using hot rocks as an IR source. Note that the volcanic emission of HCl was replaced by Ar in our modeling that does include halogens. The emission scenarios for the model studies are summarized in **Table 2**.

A first simulation emissions scenario (Eyja CO) is based entirely on observations of Allard et al. (2011). This emission contains CO but no other reduced gases such as H_2 or H_2S, which typically cannot be resolved in this experimental set up. HF was also not reported, being below detection limits. The measurements by Allard et al. (2011) yield a CO/SO_2 molar ratio of 0.175 and CO/CO_2 = 0.0044. To evaluate how the presence of CO and SO_2 impact the high-temperature chemistry of the near-source plume, sensitivity studies were undertaken that excluded CO and SO_2 from the emission (Eyja no-CO no-SO2).

A further simulation (Eyja CO–H_2-H_2S) was undertaken that included estimates for H_2 and H_2S in the Eyjafjallajökull emission (based on thermodynamic equilibrium calculations) alongside CO and the other gases reported by Allard et al. (2011). It is assumed that the magmatic gases were in thermodynamic equilibrium and at magmatic temperature on emission. For the Eyjafjallajökull summit eruption a temperature of 1273 K is assumed (Keiding and Sigmarsson, 2012). The gases obey the equilibria $CO + 0.5\ O_2 = CO_2$, $H_2 + 0.5\ O_2 = H_2O$, $H_2S + 1.5\ O_2 = SO_2 + H_2O$ with corresponding thermodynamic equilibrium constants of 1.13×10^7, 1.92×10^7, and 1.54×10^{17} at 1273 K (constants obtained from HSC). For these conditions the CO/CO_2 molar ratio 0.0044 observed by Allard et al. (2011) corresponds to an oxygen fugacity of 4.0×10^{-10} bar (i.e., QFM+1.6 log units). The corresponding H_2O/H_2 molar ratio is 387 and SO_2/H_2S molar ratio is 1379. Combining these theoretical molar ratios with the mole fraction composition for H_2O and SO_2 in **Table 2** yields estimates for the mole fractions of H_2 = 0.0024 and $H_2S = 1.45 \times 10^{-6}$ in the Eyjafjallajökull emission. Thus, it is predicted that the eruption emitted a similar quantity (by mole) of H_2 compared to SO_2, but only a trace emission of H_2S.

Some volcanoes release a larger proportion of sulfur in reduced forms. To investigate the potential impact of H_2S on the high-temperature chemistry of near-source volcanic plumes, we undertook a sensitivity study using a composition based on measurements made at Mt Etna (passive degassing) whose emission composition is still relatively oxidized, but includes H_2S (Roberts et al., 2017 and references therein) and H_2 (Aiuppa et al., 2011; **Supplementary Table S4**). We emphasize that our combination of Eyjafjallajökull plume dynamics with Mt Etna emission composition for this sensitivity study is not representative of plume chemistry for Mt Etna passive degassing conditions. Rather it reflects a possible scenario for an ash-rich explosion from Mt Etna, assuming emission composition similar to that observed during passive degassing, and plume dynamics similar to Eyjafjallajökull. The Mt Etna composition used as input to our kinetics-model study is identical to the input used for a thermodynamic model study by Martin et al. (2011) [where the H_2 emission was calculated theoretically and is somewhat higher than that observed by Aiuppa et al. (2011)]. Notably, the SO_2 content of the Mt Etna emission composition (0.029 mole fraction) is more than an order of magnitude higher than the SO_2 content of Eyjafjallajökull emission (0.002 mole fraction). The H_2S content of the emission is also much higher for Mt Etna (also with a higher ratio to SO_2), whilst the H_2, H_2O, and CO_2 mole fractions are similar (although ratios to SO_2, X/SO_2, are lower). A sensitivity study was also performed without H_2S in the Etna emission (Etna no-H_2S).

Equilibrium Modeling: HSC Thermodynamic Model

Our study compares output from the chemical kinetics model outlined above to an equilibrium model (HSC) that has been previously applied to investigate volcanic plume chemistry (e.g., Martin et al., 2006). HSC model version 7.1 was used to calculate equilibrium compositions of mixtures of air with magmatic gases under the same temperature and VA:VM boundary conditions as for the chain-of-reactors model. The input composition was determined by mixing air (composed of 78% N_2, 21% O_2 and 1% Ar) with the Eyjafjallajökull magmatic gas composition (**Table 2**) for each VA:VM, whilst temperature was specified according to the PlumeRise boundary conditions. Pure magmatic gases are usually assumed to have compositions at chemical equilibrium when they are released from the volcano (and there is good evidence for this to first order for major C- and S-bearing species, e.g., Oppenheimer et al., 2018); however, some repartitioning of Eyjafjallajökull gases may be expected for thermodynamic equilibrium calculations even at VA:VM = 0:100 because the reported gas emission composition is incomplete and the initial PlumeRise temperature is slightly lower than magmatic temperature (see section "Magmatic Gas Emissions").

RESULTS

Model Diagnostics: Cooling and Mixing of Volcanic Gases With Air

Physical parameters from the PlumeRise model (temperature T, VA:VM, distance from the source, and plume cross-sectional area) used as boundary conditions for the chain-of-reactors model vary as a function of time, **Figures 2A,B**. Temperature is varied smoothly across the chain-of-reactors and decreases from 1000 K to 890 K (over the 30 PFRs) whereas VA:VM increases stepwise from 0 to 5.3 due to air-entrainment between each reactor. This T and VA:VM scenario is not representative of all volcanoes. Smaller volcanic emissions would likely disperse faster, particularly if ash-poor. The presence of ash in Eyjafjallajökull plume maintains high temperatures at higher VA:VM than would occur in an ash-poor emission (that for example for VA:VM > 3 would yield $T < 500$ K according to simple gas-phase mixing). This result is not surprising given 1D plume-rise models of explosive eruptions typically assume an emission containing volcanic gases at a few weight-percent, with the remainder as pyroclasts. We highlight that this "temperature buffering" effect of ash may significantly prolong the period in which volcanic gases undergo high-temperature chemistry as they mix with air.

As VA:VM increases, the abundance of air-dominated gases such as O_2 increases step-wise toward an asymptote of 21% (pure air) whilst major magmatic gases such as H_2O and CO_2 decrease step-wise due to dilution, **Figure 2C**. Plume chemistry can additionally cause gas abundances to rise or fall within each reactor. **Figure 2C** shows that there is negligible or only small impact of plume chemistry on O_2, H_2O, and CO_2 whose abundances are largely controlled by air entrainment/dilution. Also shown in **Figure 2C** is the product of the O_2 and H_2O mole fractions that reaches a maximum at around 0.5 s, of relevance to the high-temperature reactions discussed in Section "Discussion."

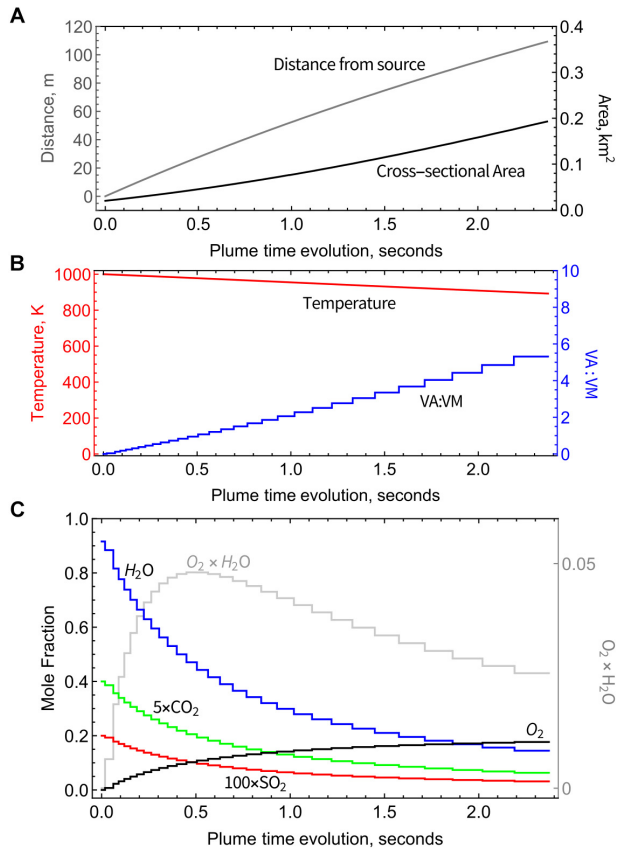

FIGURE 2 | Physical parameters used as boundary conditions for the chain-of-reactors model, from the PlumeRise model applied to Eyjafjallajökull 2010 eruption (Woodhouse et al., 2013). **(A)** Plume cross-sectional area and distance from source as a function of plume time evolution. **(B)** Decreasing temperature and increasing proportion of mixing between air and magmatic gases (VA:VM) as a function of time. **(C)** Output from the chain-of-reactors model as a function of time: mole fractions of major volcanic gases (H_2O, CO_2, and SO_2) decrease due to dilution and O_2 increases due to entrainment of background air. Also shown is the product of H_2O and O_2 exhibiting maximum around 0.5 s.

High-Temperature Production of Oxidants and Radicals

The chemical evolution of the Eyjafjallajökull near-source plume according to the high-temperature chain-of-reactors model is shown in **Figure 3A** (Eyja CO run) over a time-period of about 2.4 s, during which VA:VM increases from 0 to 5.3, and temperature decreases from 1000 K to 890 K. The slight declines in major gases H_2O, CO_2, and SO_2 mixing ratios show they are largely under the control of dilution whilst air is entrained, i.e., are largely conserved. The production of oxidant radicals such as OH, HO_2, and H_2O_2 increases rapidly with plume time evolution during the first 0.5 s, after which their absolute mixing ratios decrease. Formation of SO_3 follows a similar pattern. The volcanic gas CO decreases only slightly faster than the major gases, indicating that it is not substantially oxidized by the plume chemistry. The general pattern is similar for the Eyja CO–H_2–H_2S simulation, **Figure 3B**: a higher maximum abundance of oxidant radicals is reached (slightly earlier) and slightly more CO is oxidized, but still not completely depleted. In the Eyja CO–H_2–H_2S simulation both volcanic gases H_2 and H_2S become oxidized at around 0.5 s. To analyze the chemical kinetics model results in more detail and compare to field-observations and thermodynamic calculations, ratios are presented of the minor volcanic gases relative to the major (largely conserved) gases SO_2, CO_2, and H_2O.

Oxidation of CO Is Kinetics Limited in the Near-Source Plume

CO is only slightly oxidized by high-temperature chemistry, as shown by CO/SO_2 ratio, **Figure 4A** (as well as CO/CO_2, **Figure 4B**). At the end of the simulations (VA:VM = 5.3 after 2.4 s), CO/SO_2 has only declined by about 15% of the initial ratios for Eyja CO, and by 37% of the initial ratios for Eyja CO–H_2–H_2S. In contrast, HSC thermodynamic calculations predict near-complete oxidation of CO as soon as air is mixed with the

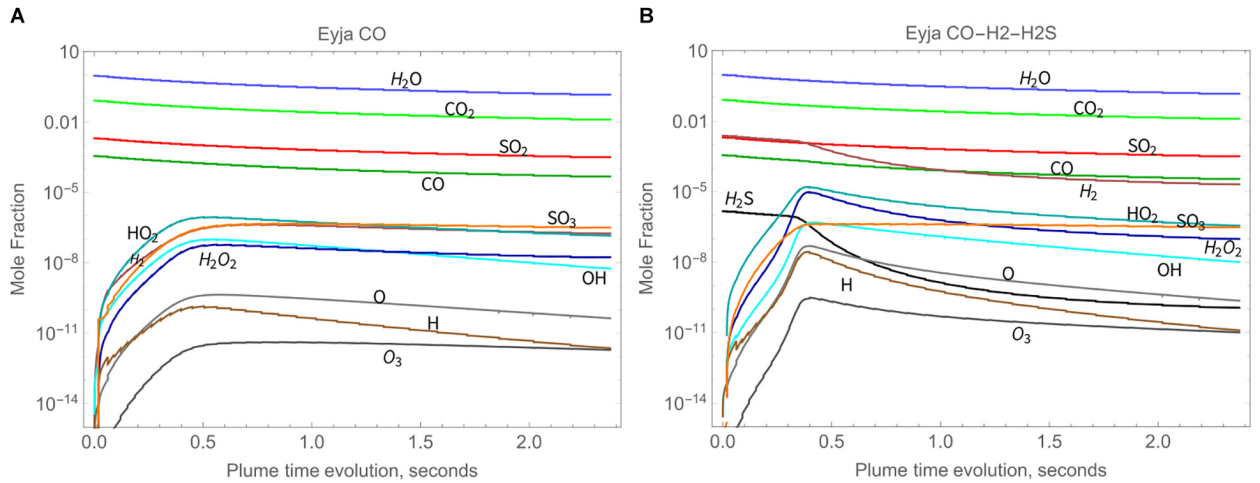

FIGURE 3 | High-temperature oxidant and radical production as a function of time in Eyjafjallajökull plume according to the chain-of-reactors model for two initial compositions, both of which include major volcanic gases H_2O, CO_2, and SO_2, as well as additional emitted gases as named: **(A)** Eyja CO and **(B)** Eyja CO-H_2-H_2S.

volcanic gases (VA:VM > 0), **Figure 4**. The kinetics model results are thus far more consistent with the presence of CO observed in the young Eyjafjallajökull plume by FTIR (Allard et al., 2011) and indeed in other volcanic gas emissions from more reduced magmas, e.g., at Mt Erebus (Oppenheimer and Kyle, 2008).

Additional observations of volcanic CO in the Eyjafjallajökull plume are reported by Schumann et al. (2011) who made instrumented aircraft measurements of the aged (10–100 h) plume over Europe during mid-April to mid-May. Both CO and SO_2 were observed above background levels. The molar ratio of excess CO and excess SO_2 (as averages) in transects of the aged plume is around ∼1, i.e., somewhat higher than the ratio reported by Allard et al. (2011) in the young plume. Reasons for this discrepancy are not clear. It is unlikely that CO was formed in the plume in an oxidizing atmosphere. Plume structure in the aircraft measurements as reported by Schumann et al. (2011) is smoother for SO_2 compared to CO. This may in part be due to the vastly different response times of the aircraft-based instruments for SO_2 (T95 response time to reach 95% signal is 80 s) and CO (response time < 2 s), which might cause a high bias in the derived CO/SO_2. There is some scatter in the CO and SO_2 measurements as well as variability in background CO. In addition, SO_2 could undergo atmospheric oxidation processes, resulting in an increase in the CO/SO_2 ratio in the downwind plume. Unusually, at Erebus volcano a rapid loss of SO_2 has been identified in the very young plume possibly aided by cloud processing (Oppenheimer et al., 2010). However, oxidation of SO_2 in volcanic plumes is typically slow (e.g., Galeazzo et al., 2018). The measurements of CO/SO_2 in the downwind Eyjafjallajökull plume do not show any clear dependency on plume age. In any case, the aircraft measurements of Schumann et al. (2011) detected volcanic plume CO alongside SO_2, confirming that CO was emitted during the 2010 Eyjafjallajökull eruption and that CO was not substantially oxidized by high-temperature near-source chemistry as is commonly predicted by thermodynamic modeling. Oxidation of CO was evidently kinetics-limited in the transient near-source plume. A summary of the model and observed CO/SO_2 is given in **Table 3**.

The Eyja CO–H_2–H_2S simulation that includes theoretical estimates for volcanic emission of H_2 and H_2S predicts near-complete oxidation of both gases, **Figure 4B**, as well as partial oxidation of CO. This is due to an oxidant enhancing feedback mechanism (see section "Discussion"). No specific observations of H_2 or H_2S are available for comparison in the Eyjafjallajökull near-source or far downwind plume. However, observations of H_2S in plumes from both passively degassing volcanoes (e.g., Roberts et al., 2017) and explosive eruption plumes (e.g., de Moor et al., 2016) indicate that H_2S is (largely) conserved, as for CO. Measurements of H_2 have been reported in plumes from some passively degassing volcanoes (e.g., Aiuppa et al., 2011; Moussallam et al., 2012). In general, observations of reduced gases in volcanic plumes (specifically CO/CO_2, H_2O/H_2, and SO_2/H_2S gas ratios) may be used to infer magmatic properties at emission such as oxygen fugacity (see section "Magmatic Gas Emissions"), on the condition that modification of the emitted composition by near-source plume chemistry is either negligible or well-constrained by plume chemistry models. Here the small decrease in CO/CO_2 predicted by the kinetics model (Eyja CO) is equivalent to a difference in oxygen fugacity of 1.5×10^{-10} bars or about 0.14 log unit QFM. We highlight two important areas of model uncertainty regarding the near-source oxidation of reduced gases. First, the reactions are temperature-dependent yet the temperature of the volcanic gas emission as well as subsequent plume physical evolution are both rather poorly known. Second, the kinetics of certain reactions, particularly for H_2S are poorly constrained by laboratory experiments. Thus, the presence of H_2 and H_2S observed in certain volcanic plumes may suggest either a lower emission temperature or faster cooling rate than the Eyjafjallajökull case presented here, or may reflect uncertainties in the model chemical schemes.

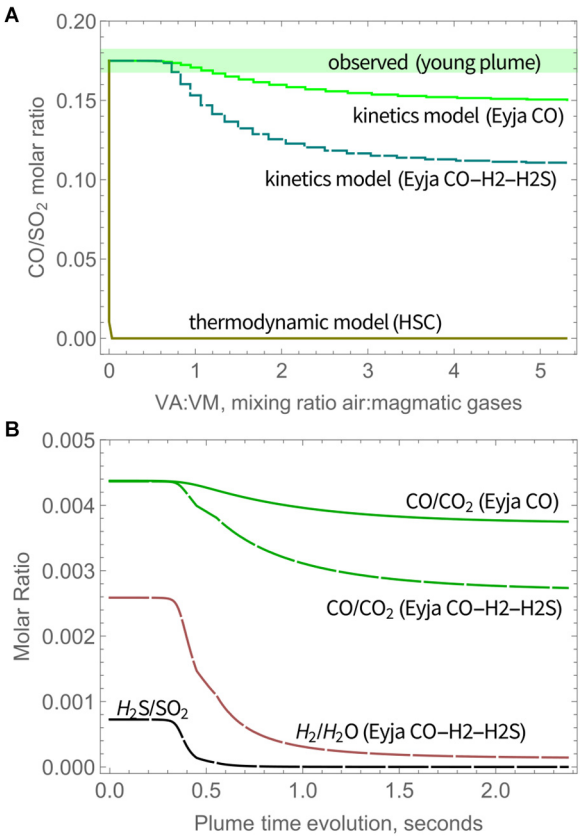

FIGURE 4 | (A) Molar ratio of CO/SO_2 in Eyjafjallajökull plume as a function of time according to the chain-of-reactors model for Eyja CO and Eyja CO-H_2-H_2S simulations, and the HSC thermodynamic model, compared to CO/SO_2 observed in the young plume by Allard et al. (2011), see also **Table 3**. Solid lines: Eyja CO simulation, Dashed lines: Eyja CO-H_2S-H_2 simulation. **(B)** Molar ratio of CO/CO_2 (Eyja CO and Eyja CO-H_2-H_2S simulations) as well as H_2S/SO_2 and H_2/H_2O (Eyja CO-H_2-H_2S simulation only) as a function of time according to the chain-of-reactors model. Solid lines: Eyja CO simulation, Dashed lines: Eyja CO-H_2S-H_2 simulation.

TABLE 3 | Molar CO/SO_2 ratio observed in Eyjafjallajokull eruption plume compared to model predictions.

Measurement/model	CO/SO_2 molar ratio
FTIR observations of the young plume on May 08, 2010 (Allard et al., 2011)	0.175
Aircraft measurements of the downwind plume on April 22, 2010 – May 18, 2010 (Schumann et al., 2011)	~1
Thermodynamic model HSC (at VA:VM = 5.3, T = 890 K)	10^{-10}
Kinetics model: Eyja CO (at t = 2.4 s, VA:VM = 5.3, T = 890 K)	0.15
Kinetics model: Eyja CO-H_2S-H_2 (at t = 2.4 s, VA:VM = 5.3, T = 890 K)	0.11

All models initialized with CO/SO_2 = 0.175.

High-Temperature Production of SO_3 as a Sulfate Aerosol Precursor

SO_3 abundance in magmatic gas is negligible but is predicted to form through high-temperature plume chemistry. SO_3 is a precursor to sulfate aerosol (as is well-known e.g., from studies of power station emissions). Upon further plume cooling, volcanic SO_3 will react readily with $H_2O_{(g)}$ to form $H_2SO_{4(g)}$ that is highly hygroscopic and will form sulfate particles. The widespread observation of near-source volcanic sulfate (see section "Introduction," **Table 1**), motivates our model investigation of high-temperature SO_3 as a possible sulfate source. The SO_3 abundance increases rapidly at around 0.5 s, **Figure 5A**. The SO_3/SO_2 molar ratio increases throughout the model simulations, indicating a continual production of SO_3 that is similar for Eyja CO and Eyja CO–H_2–H_2S. By the end of the simulations (2.4 s, VA:VM = 5.3, T = 890 K), the SO_3/SO_2 molar ratio reaches 10^{-3}. The fact that SO_3/SO_2 ratio is still increasing at the end of the model simulation indicates that additional high-temperature production of SO_3 is expected as the plume cools and dilutes further. Extrapolation of **Figure 5A** suggests SO_3/SO_2 may potentially reach up to $\sim 2 \times 10^{-3}$. Whilst there are no reported sulfate/SO_2 measurements for the Eyjafjallajökull summit eruption for specific comparison, this modeled ratio of SO_3/SO_2 of around 10^{-3} lies within the range of observed near-source sulfate/SO_2 ratios, including the Eyjafjallajökull flank eruption (**Figure 5B** and **Table 1**). In contrast, calculations using the HSC thermodynamic equilibrium model at VA:VM = 5.3, T = 890 K predict SO_3/SO_2 of around 3.1, an order of magnitude above the highest ratio of sulfate/SO_2 in the field observations, and several orders of magnitude higher than the Eyjafjallajökull observations. We conclude that the chemistry producing SO_3 in the near-source volcanic plume is under kinetic rather than thermodynamic control.

High-Temperature Production of Oxidants HO_2, OH, and H_2O_2

High-temperature oxidants HO_{xy} (HO_2, OH, and H_2O_2) are predicted to form in the Eyjafjallajökull plume through high-temperature plume chemistry, **Figures 6A,B** (absolute concentrations shown). Also shown for scale is the SO_2 concentration that decreases largely due to dilution. High-temperature HO_{xy} reaches a maximum around 0.5 s. HO_{xy} production is greater for Eyja CO–H_2–H_2S than for the Eyja CO simulation. In both cases HO_x exists predominantly as HO_2. This contrasts with thermodynamic calculations that predict HO_x to exit predominantly as OH (e.g., Gerlach, 2004). Another important feature of the chemical kinetics modeling is that H_2O_2 is predicted to form (at greatest abundance for Eyja CO–H_2–H_2S), whilst H_2O_2 is essentially not formed in HSC thermodynamic calculations (e.g., Martin et al., 2006).

High-temperature SO_3 was discussed above as a precursor to sulfate aerosols. The H_2O_2 formed by high-temperature chemistry may promote further sulfate formation upon plume cooling, due to its reaction with dissolved $SO_{2(aq)}$. If a condensed phase is formed already in the crater zone this could yield an additional source of "primary" or near-source sulfate. Alternatively, if plumes become condensed clouds further

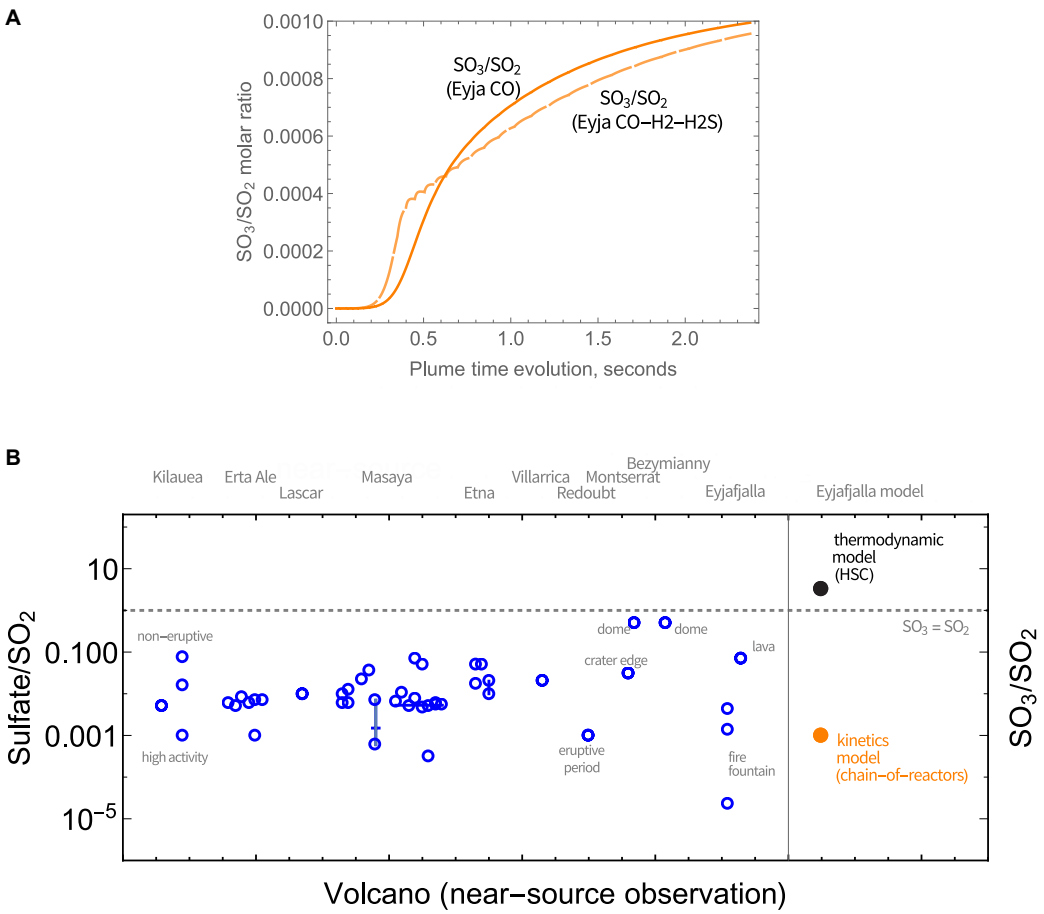

FIGURE 5 | (A) Evolution in the SO_3/SO_2 molar ratio in Eyjafjallajökull plume as a function of time, according to the chain-of-reactors model. Solid lines: Eyja CO simulation, Dashed lines: Eyja CO-H_2-H_2S simulation. **(B)** Observations of near- or at-source sulfate relative to SO_2 reported in volcanic plumes (**Table 1**) compared to the molar ratio of sulfate precursor SO_3 to SO_2 predicted by the chain-of-reactors model for Eyjafjallajökull eruption plume (time = 2.4 s, T = 890 K, VA:VM = 5.3) and HSC thermodynamic equilibrium calculations for the same plume conditions (T = 890 K, VA:VM = 5.3). The SO_3 = SO_2 is demarked by a dotted line.

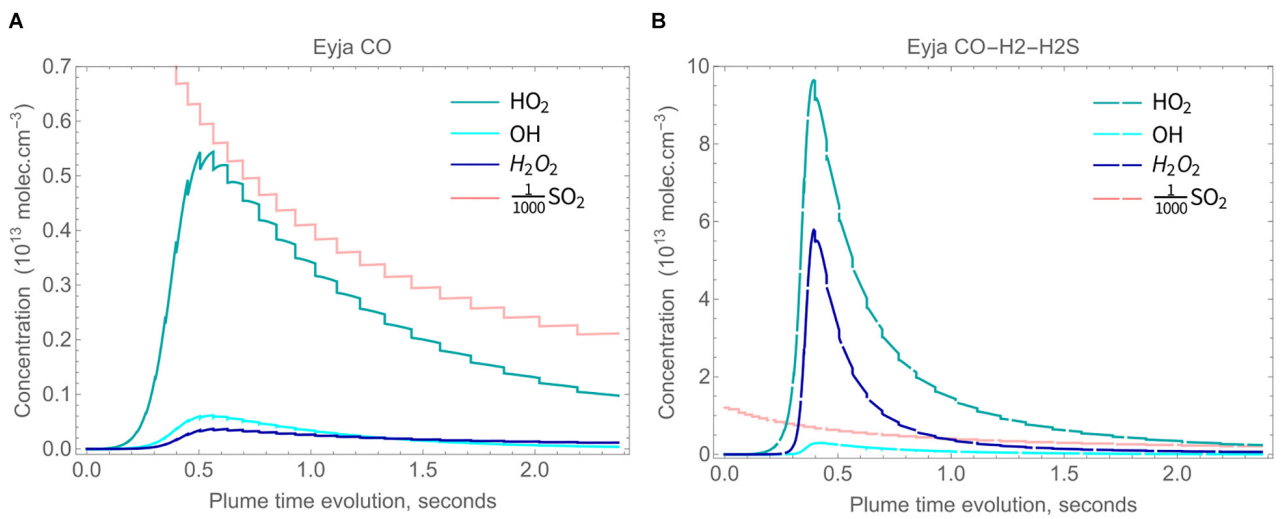

FIGURE 6 | Concentrations of HO_2 (blue), H_2O_2 (dark blue) and OH (cyan) in the plume, with SO_2 concentration also shown for scale, molec cm^{-3}. **(A)** solid lines: Eyja CO simulation and **(B)** dashed lines: Eyja CO-H_2-H_2S simulation.

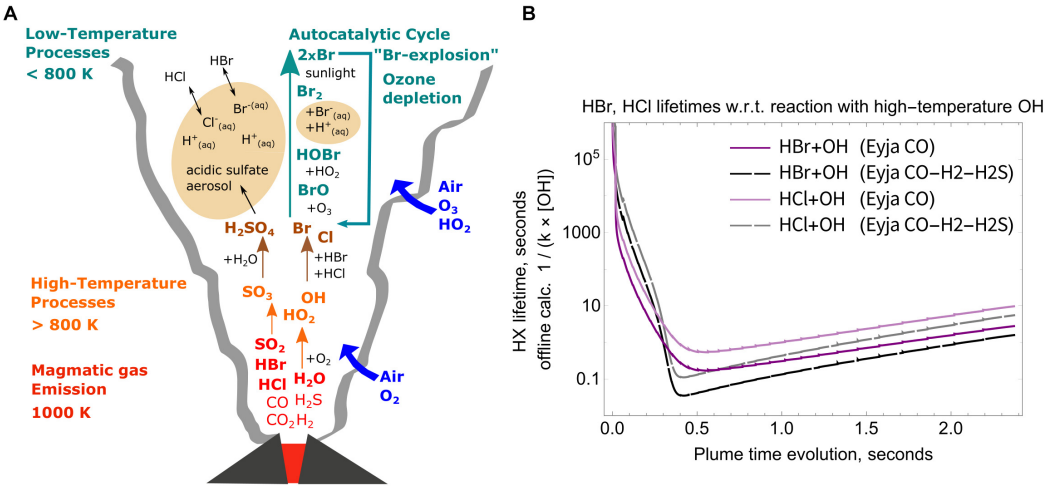

FIGURE 7 | (A) schematic of key high-to-low temperature processes in the volcanic plume, including high-temperature production of SO_3 as sulfate aerosol precursor, HOx oxidants and halogen radicals, and low-temperature multi-phase chemistry producing BrO. **(B)** Calculated lifetimes of HCl and HBr in the plume with respect to their reaction with high-temperature OH as a function of plume evolution time. Solid lines: Eyja CO simulation, Dashed lines: Eyja CO-H_2-H_2S simulation. Lifetime minima are <1 s, see **Table 4**.

downwind, the volcanic H_2O_2 may form secondary sulfates. In this respect, Carn et al. (2011) measured H_2O_2 in the plume emitted by Huila volcano (elevated above background by about 0.5 ppbv) that was rapidly titrated when the plume entered a cloudy phase. We are unaware of other observations of H_2O_2 in volcanic plumes.

We highlight two further potential impacts of volcanic H_2O_2. Studies have shown that iron on the surface of volcanic ash has the potential to generate substantial quantities of hydroxyl radicals that may affect the toxicity of inhaled ash particles (Horwell et al., 2003; Hillman et al., 2012). This occurs via the Fenton reaction involving H_2O_2. The elevated abundance of H_2O_2 in the volcanic plume predicted by our model study would likely enhance the production of OH radicals and their potential health hazard. Indeed, an observation that has puzzled the volcanology-atmospheric community to date is the presence of elevated OH (and HO_2) measured in the 2010 Mt Hekla eruption cloud in the stratosphere (Rose et al., 2006). This elevated OH is all the more surprising given the measurement was made during night-time and in the presence of major OH reactive sinks (e.g., HCl and SO_2). We propose the reaction of volcanic H_2O_2 on ash particles as a possible mechanism that could generate OH radicals in volcanic plumes even during night-time.

Potential for High-Temperature Formation of Halogen Radicals

High-temperature oxidants such as OH and radicals such as Br, Cl are believed to have an important role in accelerating the onset of low-temperature atmospheric chemistry "bromine explosion" cycles that form BrO and destroy ozone in the downwind plume (e.g., Bobrowski et al., 2007; Roberts et al., 2014; Surl et al., 2015; **Figure 7A**). The bromine explosion is autocatalytic so can be efficiently "kick-started" by a small quantity of high-temperature halogen radicals. Observations show that halogens were emitted during the eruption (young plume $HCl/SO_2 \approx 0.65$, Allard et al., 2011) and that reactive halogen chemistry was active in the plume (downwind plume $BrO/SO_2 \approx 1.3 \times 10^{-4}$, Heue et al., 2011). The Eyjafjallajökull volcanic halogen chemistry caused a depletion of tropospheric ozone (Vance et al., 2010; Schumann et al., 2011). Here offline calculations show the potential for formation of high-temperature halogen radicals to initiate this process.

The OH formed in the near-source volcanic plume is a powerful oxidant that can react with volcanic halogens (emitted as HCl and HBr) to produce halogen radicals (R1 and R2). The high-temperature chemical kinetics model scheme used in this study does not include halogen chemistry. Nevertheless, offline calculations of the lifetime of volcanic HCl, HBr emissions can be undertaken to estimate the potential for halogen radical formation, shown here for the Eyjafjallajökull simulations.

$$\text{R1} \quad HCl + OH \rightarrow Cl + H_2O$$

With bimolecular rate constant reported by Ravishankara et al. (1985) as $k = 4.5 \times 10^{-17} \times T^{1.65} \exp[112/T]$ cm^3 $molecule^{-1}$ s^{-1} (valid for 240–1055 K).

$$\text{R2} \quad HBr + OH \rightarrow Br + H_2O$$

With bimolecular rate constants estimated by Góger et al. (2018) as $k = (9.86 \pm 2.38) \times 10^{-16} \times T^{(1.23 \pm 0.03)} \times \exp[(5.93 \pm 0.33)$ kJ $mol^{-1}/RT]$ cm^3 $molecule^{-1}$ s^{-1} (valid for 600–3200 K).

Lifetimes of HBr and HCl in the near-source plume are calculated by the inverse of the first-order rate constant, i.e., the product of the 2nd order rate constants for R1 and R2 with the OH concentration. The temperature dependence of the rate constants is only slight (variation of up to about 15%) over our studied temperature range 890–1000 K. Rather, **Figure 7B** shows that the calculated HCl and HBr lifetimes during the Eyja

TABLE 4 | Simulated maximum OH/SO_2 ratio and OH concentration in the high-temperature near-source plume according to the chain-of-reactors model, and minimum lifetime of HX (X = Br or Cl) with respect to reaction with OH by offline calculation (see section "Potential for High-Temperature Formation of Halogen Radicals" and **Figure 7B**).

Model run	Maximum OH/SO_2 (simulated) mol/mol	Maximum OH concentration (simulated) molec cm^{-3}	Minimum HBr lifetime (offline calculation) seconds	Minimum HCl lifetime (offline calculation) seconds
Eyja CO	1.06×10^{-4}	6.13×10^{11}	0.167	0.534
Eyja CO-H_2-H_2S	4.38×10^{-4}	2.93×10^{12}	0.035	0.110

For comparison, the observed Eyjafjallajökull plume HCl/SO_2 and BrO/SO_2 molar ratios are 0.6 and $\approx 1.3 \times 10^{-4}$, respectively, and the total time-duration of the high-temperature simulation is 2.4 s.

CO and Eyja CO–H_2–H_2S simulations are a strong function of OH concentration. The halogen halide lifetimes rapidly decrease as OH is formed in the near-source plume, and then increase as OH is consumed (and diluted). Lifetimes of HBr and HCl reach minima of <1 s in the plume, **Table 4**. Lifetimes are shortest for HBr that has the greater rate constant of reaction and for the Eyja CO–H_2–H_2S simulation that produces highest OH concentration. In all cases, the calculated HBr and HCl lifetime minima are shorter than the timescale of the plume simulation (2.4 s) indicating that significant halogen radical production will occur. Reactions R1 and R2 will likely cause a negative feedback on OH concentrations. Once formed the halogen radicals will react with CHOS and some may reform HBr or HCl. A more comprehensive understanding of the halogen interactions will require inclusion of halogen reactions explicitly in the high-temperature model chemical mechanism.

DISCUSSION

Chemical Reaction Mechanisms and Feedbacks

The chemical kinetics model identifies key reactions causing oxidation and oxidant production in the volcanic plume. In this study, the model simulations predict abundances of oxidants, and oxidized species increase rapidly around 0.5 s, at T = 980 K, corresponding to VA:VM around 1 according to the specific Eyjafjallajökull boundary conditions scenario used (different times or temperature conditions can be expected under other plume dyamics conditions). VA:VM = around 1 corresponds to the point where mixing of magmatic gases and air yields a maximum in the product of air-derived O_2 and magmatic-derived H_2O. Radical oxidants HO_x are produced from the reaction of H_2O with O_2 to form OH and HO_2, R3. This (two-way) reaction usually acts as a sink rather than source of radicals in combustion but OH and HO_2 formation in the near-source volcanic plume is driven by the unusually high H_2O content of the plume-air mixture at high temperatures. Production of HO_x is fastest at around 0.5 s or VA:VM = 1, coincident with the maximum in the product of H_2O and O_2 mole fractions.

$$\text{R3} \quad H_2O + O_2 \rightleftharpoons OH + HO_2$$

Formation of SO_3 occurs by the reaction R4 of SO_2 with HO_2.

$$\text{R4} \quad SO_2 + HO_2 \rightleftharpoons SO_3 + OH$$

When CO is present in the plume, some of it can react with OH to form CO_2 and H radicals, R5, which may further react with O_2 to form HO_2, R6.

$$\text{R5} \quad CO + OH \rightleftharpoons CO_2 + H$$

$$\text{R6} \quad H + O_2 + M \rightleftharpoons HO_2 + M$$

Once formed, HO_2 can react with itself, R7, to produce hydrogen peroxide, H_2O_2.

$$\text{R7} \quad HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$$

Some H_2O_2 can also thermally decompose to form OH radicals, R8.

$$\text{R8} \quad H_2O_2 + M \rightleftharpoons OH + OH + M$$

In high-temperature chemistry (generally temperatures above 800–850 K), formation of H_2O_2 is usually considered as a sink of oxidant radicals. However, in the case of a near-source plume the removal of OH by CO (R5, followed by R6 and R7 leading to H_2O_2) drives the formation of more OH and HO_2 from the reaction of H_2O with O_2 (more specifically, the balance of this reaction, R3, with its reverse reaction). This feedback mechanism promotes the production of HO_{xy} in volcanic plumes containing CO, where only a fraction of the emitted CO needs to be oxidized to substantially enhance HO_{xy} abundances and promote the chain reaction. Similarly, the H_2 emission in the Eyja CO–H_2–H_2S simulation can also react with OH, R9 (followed by R6 and R7) to cause a similar positive feedback on HO_x production.

$$\text{R9} \quad H_2 + OH \rightleftharpoons H_2O + H$$

These feedbacks involving reduced gases may explain the greater production of oxidants in Eyja CO–H_2-H_2S than Eyja CO simulation. This hypothesis is supported by a sensitivity study without CO and SO_2 in the emission (Eyja no-CO no-SO_2, **Supplementary Figure S2**) that produces a lower OH abundance but where more OH accumulates more in the first hundreds of milliseconds, reflecting the balance of OH production and consumption.

We now consider the role of H_2S. The very low (theoretically estimated) H_2S emission from Eyjafjallajökull had a rather negligible impact on the near-source plume chemistry. The role of H_2S is investigated in a simulation of the high-temperature chemistry of Mt Etna emissions, that include H_2 and H_2S as well as SO_2, H_2O, and CO_2, see **Supplementary Table S4** (as well as

a control run that excludes H_2S). The Etna simulation assumes an eruption with the same plume physics as for Eyjafjallajökull. A very rapid production of oxidants is predicted within the first 0.1 s of plume evolution, **Supplementary Figure S3**, coincident with a rapid decrease in H_2S (and a slower decrease in H_2). Abundances of oxidant radicals initially substantially exceed those predicted for Eyja CO and Eyja CO–H_2–H_2S, and later decline to lower levels. According to our model, the oxidation of emitted H_2S causes an extra production of O atoms (which is not observed in the case "without H_2S") with in the first milliseconds of the plume's mixing with air, following the sequence: $H_2S + H$ (or OH) = $SH + H_2$ (or H_2O), $2SH = H_2S + S$, $S + O_2 = SO + O$, and $SO + O_2 = SO_2 + O$. The production of sulfur atoms from H_2S and their subsequent reactions with O_2 are mostly responsible for this production of O, which, in turn, converts SO_2 into SO_3, resulting in the SO_3 peak observed at 0.1 s in the plume. Beyond this point, the conversion of SO_2 into SO_3 is mainly due to the abundance of HO_2 through $SO_2 + HO_2 = SO_3 + OH$. A significant part of SO_3 is then used to recycle SO_2 through the formation of $HOSO_2$ ($SO_3+HO_2 = HOSO_2+O_2$ and $HOSO_2+M = SO_2+OH+M$). Indeed, the formation of SO_3 in the Mt Etna scenario proceeds through two different mechanisms (with O, and then with HO_2) at different locations in the plume whereas in the Eyja CO and Eyja CO-H_2-H_2S or Etna no-H_2S scenarios, the formation of SO_3 is only linked to HO_2. It must be emphasized, however, that model predictions are limited by uncertainty in high-temperature H_2S chemistry.

This sulfur cycling regulates SO_3/SO_2 to reach around 10^{-3} after 2.4 s in all of the simulations (Eyja CO, Eyja CO-H_2-H_2S, Etna and Etna no-H_2S, **Figure 5A** and **Supplementary Figure S3**), despite their differences in CO-H_2-H_2S emissions that lead to vast differences in the production and abundances of HO_{xy}. Temperature and VA:VM evolution with time may be important controls on SO_3/SO_2, therefore production of near-source sulfate could vary for different physical conditions other than the Eyjafjallajökull case considered here.

Model Uncertainties and Future Directions

Our chain-of-reactors model provides a framework for quantitative studies into the high-temperature reactions occurring in the near-source plume to form oxidized products such as sulfate-precursors, OH, H_2O_2 that can impact subsequent physico-chemical processing in the cooled plume. We find that the high-temperature chemistry is under kinetic control; plume composition does not follow thermodynamic equilibrium (**Figures 4A**, **5B**, with example model output in **Supplementary Tables S5, S6**). Our exploratory study identifies several areas for further investigation.

Improved Model Chemistry at High-Temperatures and Link to Low-Temperature Plume Processes

Uncertainties in the high-temperature gas chemistry mechanism need to be addressed such as the chemical kinetics of sulfur species reactions, notably the oxidation of H_2S, that are poorly quantified from laboratory experiments. Future model developments should also incorporate the chemistry of halogens and nitrogen species coupled to CHOS. Simulations of longer duration should cover the whole regime where high-temperature chemical reactions may be important (e.g., down to 800/850 K). The gas-phase mechanism should be extended to consider photolysis reactions for plumes that are not too optically thick, and, especially, heterogeneous chemical reactions, for example reactions on ash surfaces (Delmelle et al., 2018), noting the oxidized products from high-temperature gas chemistry could act to modify ash properties. Models should ultimately be developed that encompass both high-temperature chemistry and also the transition to low-temperature plume chemistry as simulated by atmospheric models (e.g., Jourdain et al., 2016).

Influence of Emitted Magmatic Gas Composition on High-Temperature Chemistry

The composition of magmatic gases released is specific to each volcano and can vary with volcanic activity/unrest. The chemical feedback mechanisms identified by our model suggest that emissions of reduced gases can enhance the high-temperature production of oxidants. This might lead to a greater production of oxidant radicals in the near-source plume of volcanoes with a relatively reduced emissions composition, such as Mt Erebus, Antarctica, whose emissions are rich in CO and H_2. Few field-measurements exist to evaluate model predictions: the high-temperature region is difficult to access directly and few studies have quantified oxidized products in the cooled downwind plume, e.g., by instrumented aircraft. Another critical uncertainty is that the emission temperature of volcanic gases is poorly known. In some situations, according to the dynamics of the degassing, magmatic gas emissions at the surface may be neither in chemical nor thermodynamic equilibrium with the melt (Oppenheimer et al., 2018).

Influence of Plume Dynamics on High-Temperature Chemistry

The chemical kinetics model requires time-resolved boundary conditions in plume dynamics, notably temperature and VA:VM (degree of mixing of air with magmatic gases). This study used output from a 1D PlumeRise model for the Eyjafjallajökull 2010 eruption (Woodhouse et al., 2013) for this purpose. Variability in plume dynamics was not investigated but is expected to exert a strong influence on the near-source chemistry through the rate of entrainment of air and cooling. For example, smaller emission sources will typically disperse and cool faster in the troposphere. Ash-poor emissions will tend to cool more rapidly than ash-rich emissions where the solid pyroclasts buffer the temperature of the volcanic gas and air mixture. Large eruptions that inject gases and ash into the stratosphere should also be investigated. Spatial heterogeneity in the turbulent mixing of air into the plume might non-linearly impact the plume chemistry, potentially requiring the development of 3D model approaches to investigate the plume's high-temperature chemistry as a function of a more detailed turbulent mixing.

CONCLUSIONS

We present chemical kinetics model simulations of the high-temperature gas chemistry that occurs as magmatic gases mix with air and cool in the near-source volcanic plume. Volcanic gases released into the atmosphere undergo rapid processing including photochemistry, oxidation, and aerosol formation. Quantifying these processes in volcanic plumes is essential to assess atmospheric and environmental impacts of volcanic emissions. During the first few seconds after release, the hot magmatic gases mix with background air containing oxidants and undergo a high-temperature processing. The gas chemistry in this high-temperature region of the plume is poorly characterized, yet can critically modify the composition of the emission to produce oxidized products and radicals, such as near-source sulfates, HOxy, and halogen radicals. These high-temperature products influence the subsequent physico-chemical processing of the plume at low-temperatures as it disperses in the atmosphere. Studies to date have largely represented the chemical composition of the high-temperature region using thermal equilibrium calculations (e.g., Martin et al., 2006; Hoshyaripour et al., 2012). A source of uncertainty in thermodynamic modeling of the high-temperature chemistry of volcanic plumes is the assumption of equilibrium conditions, that may not always be valid for transient plumes (Martin et al., 2009).

The chain-of-reactors approach of this study is time-resolved and based on chemical kinetics thus differs markedly from thermodynamic equilibrium calculations used to date. We performed an exploratory study of the high-temperature chemistry in a near-source volcanic plume over the first 2.4 s, using as boundary conditions for the time-varying temperature and mixing of air output from 1D PlumeRise model simulations of Eyjafjallajökull plume (Woodhouse et al., 2013). The magmatic gas emission includes H_2O, CO_2, SO_2, and CO, based on observations of the young plume (Allard et al., 2011), with theoretical estimates for H_2S and H_2 gas emissions added in a sensitivity study and offline calculations performed for halogens.

A key finding is that the plume chemistry is under kinetic control and that thermodynamic equilibrium cannot be assumed. The simulation predicts that CO emission from Eyjafjallajökull is not fully oxidized (largely conserved) by high-temperature chemistry. This is consistent with field-observations of CO in the volcanic plume (Allard et al., 2011; Schumann et al., 2011) and contrasts to thermal equilibrium calculations of near-complete CO oxidation, **Table 3**. Instead, our study shows CO oxidation is under chemical kinetics control. The model predicts that sulfate-precursor SO_3 is formed at levels ($SO_3/SO_2 = 10^{-3}$) in general agreement to observations of near-source volcanic sulfate/SO_2 in volcanic plumes, **Table 1**. Conversely, thermodynamic calculations predict a much greater formation of SO_3 relative to SO_2 for the same plume dynamics conditions. The kinetics model predicts high-temperature formation of HO_2, OH, and H_2O_2. Formation of HO_{xy} is predicted to be enhanced when additional reduced gases (H_2S and H_2) besides CO are included in the emission.

Offline calculations demonstrate that volcanic halogens (HBr and HCl) will react rapidly with high-temperature OH, highlighting the potential for halogen radicals to form in the high-temperature plume. A key chemical mechanism is that HO_x oxidants are formed by the (reversible) reaction of H_2O with O_2 at high-temperatures to produce OH and HO_2. Chemical feedbacks occur when reduced gases in the volcanic emission (CO and H_2) react with OH to produce HO_2 that can self-react to form H_2O_2. Thus reduced gases in the volcanic emission act to promote formation of high-temperature HO_{xy}. Another chemical feedback occurs via the oxidation pathway for volcanic H_2S that rapidly generates additional oxidants in a chain-reaction. However, there is large uncertainty in some high-temperature reactions, particularly for sulfur species. Quantifying the chemical processes occurring at high-temperatures in the near-source plume is an essential step in understanding the reactivity and evolution of volcanic emissions and their impacts in the troposphere and stratosphere. Improved characterization of this high-temperature region of the plume will require the combination of model, field-observation and laboratory studies.

AUTHOR CONTRIBUTIONS

All authors contributed to the study design, analysis and interpretation of data, and manuscript writing.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2019.00154/full#supplementary-material

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