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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 HOx) 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.

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