

The enigma of reactive nitrogen in volcanic emissions

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Nitrogen fixation has been reported at numerous active volcanoes. Where it occurs, it should enhance nitrogen bioavailability in the local environment and reactive nitrogen chemistry in the troposphere. Measurements of reactive nitrogen species in volcanic emissions are highly variable, in part due to an incomplete assessment of a diverse speciation (e.g., NO, NO₂, HNO₃, NO₃⁻ and NO₂HO₂), but suggest typical molar ratios of NO_y/H₂O = 10⁻⁵. These high levels of reactive nitrogen species may be explained by equilibrium in high temperature (>1000 C) mixtures of magmatic and atmospheric gases. However, using a kinetic model for a simplified magmatic and atmospheric gas mixture (i.e., the C-O-N-H-Ar system), we show that the rate of thermal nitrogen fixation is too slow for equilibrium to be attained in transient mixtures forming at volcanic vents. Other mechanisms for high NO_y/H₂O should therefore be considered including the catalysis of nitrogen fixation by metal salts. Our results also suggest that H₂ and CO should oxidise extremely rapidly (<10⁻³ s at 1100 C) at volcanic vents, conflicting with recent measurements indicating the stability of these reduced species. We therefore propose that high temperature oxidation at volcanic vents is a sporadic process due to variability in the mixture lifetime (with time and across the mixing front between magmatic and atmospheric gases). This variability would result in minimal losses of H₂ and CO while still allowing oxidised trace species (e.g., NO, OH, Br, Cl) to form in significant concentrations and thus influence the chemical evolution of the volcanic plume at ambient temperatures.