

Near-source observations of bromine oxide indicate oxidation of magmatic gases at the magma-atmosphere interface

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Nies et al., 2025. Reactive bromine in volcanic plumes confines the emission temperature and oxidation of magmatic gases at the atmospheric interface. *Sciences Advances*.

Contrasting community viewpoints on high-temperature plume chemistry

Geoscience perspective

- Eruption Hazard Monitoring
- Magmatic gases are a "telegram" from Earth interior
- Redox ratios represent oxidation state of the magma
- Assume volcanic gas emissions are largely unreactive on entering the atmosphere

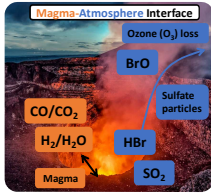


Fig. 1) Chemistry at the magma-atmosphere interface [1]

Atmospheric plume perspective

- Chemistry-Climate Impacts
- Volcanoes emit special cocktail of gases highly reactive in the atmosphere
- Example: BrO explosion and catalytic destruction of atmospheric O₃
- Reaction cycle shows oxidative capacity of early stage volcanic plumes - hot volcanic plumes are highly reactive

Our novel model of hot plume gas chemistry resolves that problem!

Combustion-Atmospheric model - kinetic chemistry model from the magma-atmosphere interface towards downwind plume chemistry

- 2 stage kinetic box model including C-H-O-N-S-Cl-Br-Hg chemistry [2]
- Solving chemical kinetics alongside turbulent mixing and dilution trajectory [3]
- 2 chemical mechanisms accounting for high-temperature (HT stage) and atmospheric chemistry (ATM stage)
- Chemical mechanism compiled with python open software package CANTERA [4]
- Identify dominant reactions through reaction path analysis
- HT stage: gas-phase chemistry + photolysis (113 species and 646 reactions) [5-8]
- ATM stage: gas-phase chemistry + photolysis + simplified heterogeneous chemistry (mainly BrO explosion)
- Both model stages run fast (< 2s) to test large range of initial parameters (e.g. mixing scenarios, gas composition and initial gas temperatures)

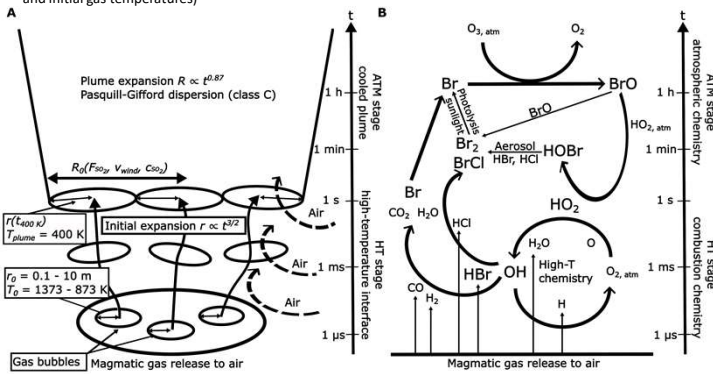


Fig. 2) Overview over the physics (A) and chemistry (B) implemented in the combustion-atmospheric model

Summary: Hot volcanic emission plumes are chemically highly reactive

- Tracing chemical evolution of a volcanic plume from hot emission until cooled downwind halogen processing of BrO
- HO₂ radical activation is a key driver for plume chemistry at the magma-atmosphere interface
- Magmatic gas emission temperature T₀ controls HO₂ formation
- Near-source presence of BrO in volcanic plumes gives lower limit for T₀
- Persistence of reduced species (e.g. H₂) gives upper limit for T₀
- ➔ BrO in near-source volcanic plumes indicates strong oxidative processing at the magma-atmosphere interface

Chemistry Model + Observations (BrO + H₂/H₂O)

Constrains magmatic gas emission temperature T₀

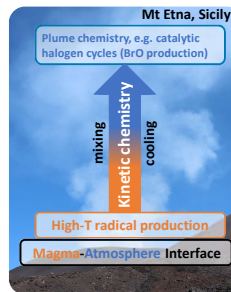


Fig. 6) Kinetic chemistry linking the magma-atmosphere interface to downwind plume chemistry as for example BrO formation.

References

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Case study: Emissions from Mt Etna, Sicily, Italy

Fast redox chemistry at the magma-atmosphere interface

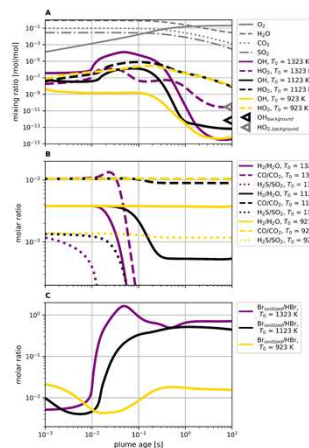


Fig. 3) Fast redox chemistry in the HT stage of the combustion-atmospheric model. Panel A shows the formation of HO₂ radicals (OH and HO₂), panel B the fate of redox couples (H₂/H₂O, CO/CO₂, H₂S/SO₂), and panel C the formation of oxidized bromine species Br_{oxidized}

High-temperature formation of reactive halogen species and subsequent downwind formation of BrO

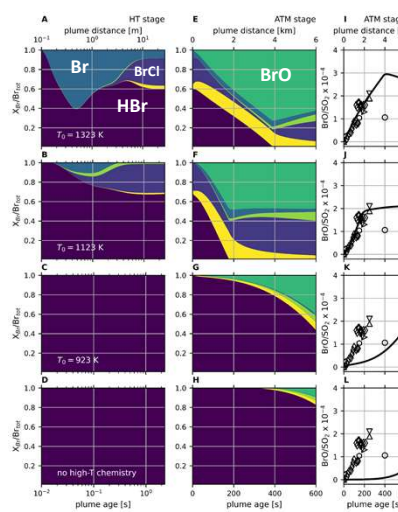


Fig. 4) Formation of reactive bromine species in both stages of the combustion-atmospheric model. The four rows show different initial magmatic gas temperatures T₀. The two first columns show the relative bromine speciation in the HT and ATM stages and the last column the BrO/SO₂ ratio compared to observations [9].

Oxidation of magmatic gases at the magma-atmosphere interface - implications for the emission temperature of magmatic gases

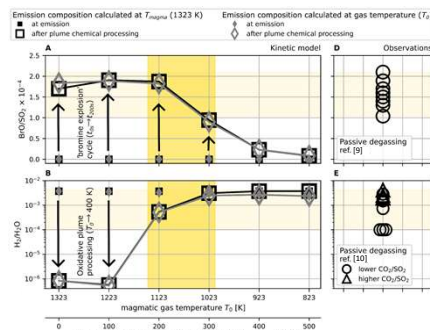
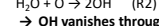
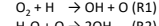


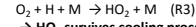
Fig. 5) Comparison of model results (first column) with observations (second column). Shown are 6 model runs with different initial magmatic gas temperatures T₀. The closed symbols show the magmatic gas composition prior to emission to the atmosphere and the open symbols are the model results in the cooled downwind plume after chemical processing at the magma-atmosphere interface.

High-T formation of OH (up to ppm levels)



➔ OH vanishes through cooling and oxidation of reduced plume species (e.g. CO, H₂)

Low-T formation of HO₂



➔ HO₂ survives cooling process

Fast redox chemistry of H₂, CO, and H₂S

➢ Strong oxidation of reduced species for T > 1100 K

➢ Mainly by reaction with OH

➢ Subsequent production of H and subsequent OH formation by (R1)

➔ T₀ < 1100K survival of reduced species

Formation of oxidized/reactive bromine species

➢ Fast oxidation of HBr by OH (t < 0.1 s)

➢ Strong temperature dependency of oxidized Br species

➔ Significant formation of oxidized Br species for magmatic gas emission temperature T₀ > 1000 K

Formation of reactive bromine species at the magma-atmosphere interface (HT stage)

➢ Relative abundance of bromine species (X_{Br}) to total bromine (Br_{tot})

➢ Up to 40% conversion to reactive bromine after HT stage

➢ Strong dependency on magmatic emission temperature T₀

➢ Dominant species: Br and BrCl

Atmospheric chemistry halogen cycles (ATM stage BrO explosion)

➢ Reactive species from HT stage (HO₂, Br, BrCl etc.) kickstart atmospheric halogen cycles (BrO explosion)

➢ HT stage chemistry essential for fast BrO formation

➔ BrO formation depends on magmatic gas emission temperature T₀

Comparison of BrO and H₂/H₂O measurements to model results

➢ measure of model BrO and H₂/H₂O ratio at emission and after chemical processing at the magma-atmosphere interface

➢ For T₀ < 1050 K: emission redox ratio of H₂/H₂O is preserved into the cooled plume

➔ H₂/H₂O constrains magmatic gas emission temperature T₀ (upper limit of 1150 K)

➢ For T₀ > 1000 K: BrO similar to observations

➔ BrO constrains magmatic gas emission temperature T₀ (lower limit of 1000 K)

Career Note

I am currently seeking postdoctoral opportunities in gas geochemistry of volcanic emissions and related research fields, with immediate availability. Please feel free to contact me during the conference or by email at alexander.nies0795@gmail.com.

