Trace H_2S Promotes Organic Aerosol Production and Organosulfur Compound Formation in CO_2-CH_4-N_2 Haze Chemistry

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INTRODUCTION

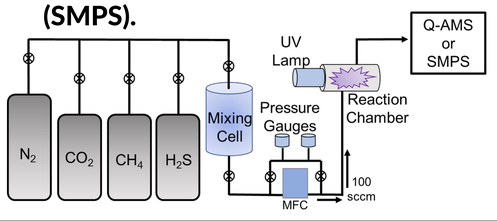
- Organic haze of Archean Earth likely influenced climate and habitability
- Sulfur isotopes best constraint on O_2 levels during Archean eon
- Current view of Archean atmosphere generally separates CO_2-rich organic haze chemistry and atmospheric sulfur chemistry
- Volcanic/biological H_2S were likely present in the Archean atmosphere.[1,2,3]

OPEN QUESTIONS

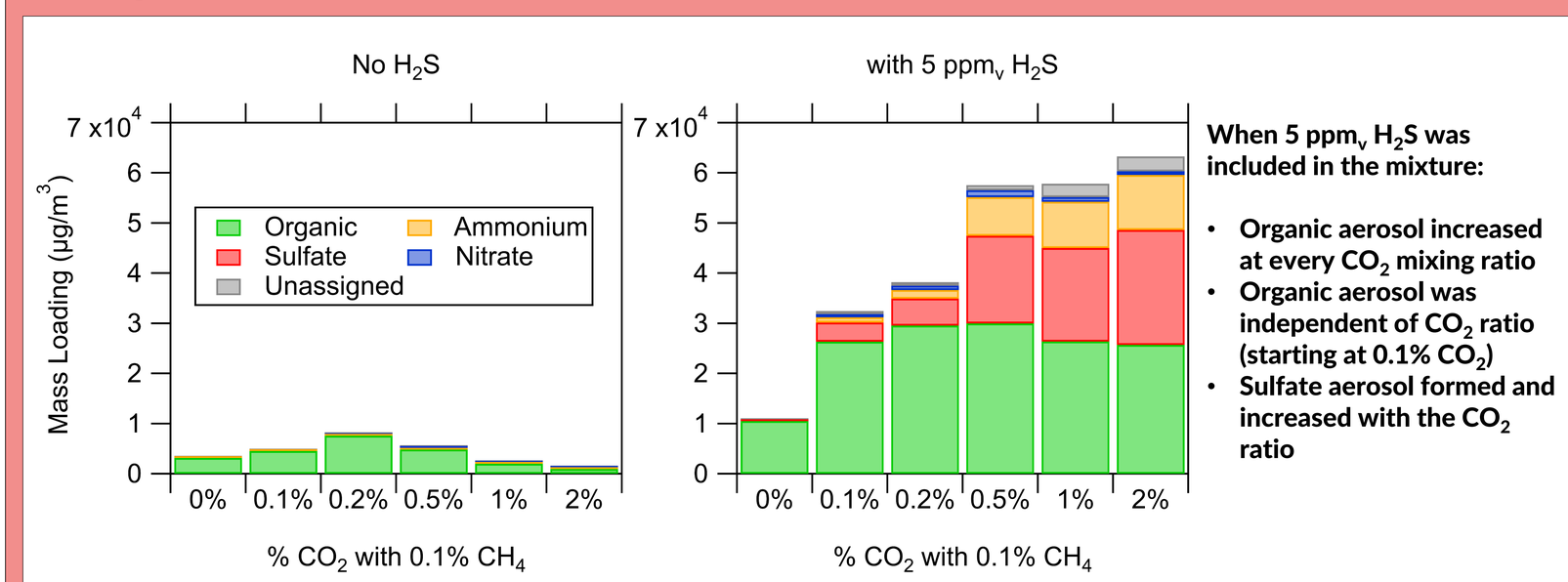
- What is the interplay between H_2S and haze chemistry? How does this change as a function of CO_2?
- Could H_2S enhance organic aerosol production at high CO_2 mixing ratios (CO_2:CH_4 > ~1) as it does in CO_2-free experiments?[4]
- How could this chemistry affect our understanding of Archean atmospheric sulfur and haze chemistry?

METHODS

- Generate haze particles from gas mixtures with 5 ppm_v H_2S, 0.1% CH_4, and 0.1-2% CO_2 in N_2 via a flow system and UV reaction cell.[4]
- Measure the particle mass loading and composition in real time with quadrupole aerosol mass spectrometry (Q-AMS) and a Scanning Mobility Particle Sizer (SMPS).

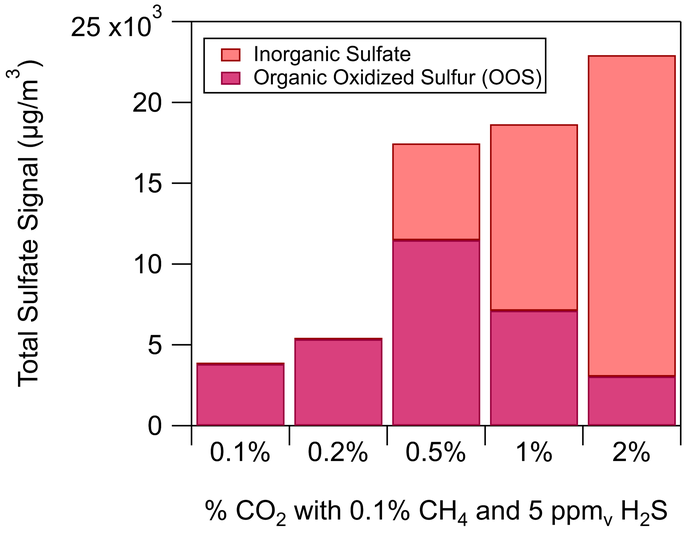


Addition of trace H_2S to early Earth haze analog experiments ***increased*** organic aerosol production and produced ***inorganic <u>and</u> organic sulfate*** aerosol

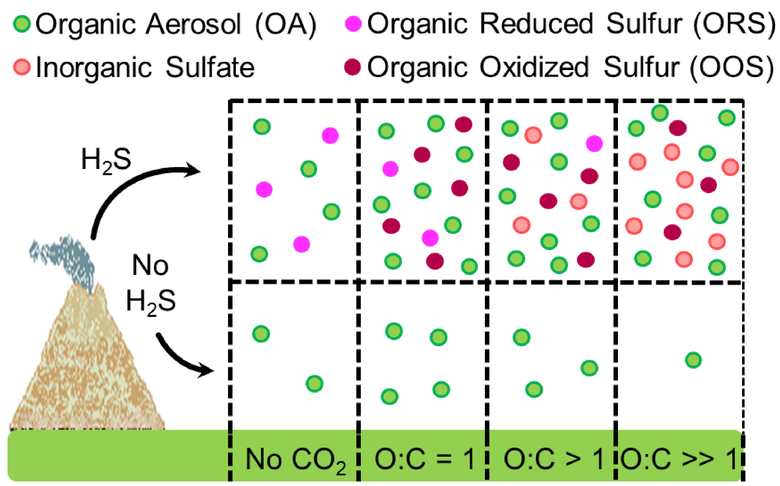


When 5 ppm_v H_2S was included in the mixture:

- Organic aerosol increased at every CO_2 mixing ratio
- Organic aerosol was independent of CO_2 ratio (starting at 0.1% CO_2)
- Sulfate aerosol formed and increased with the CO_2 ratio



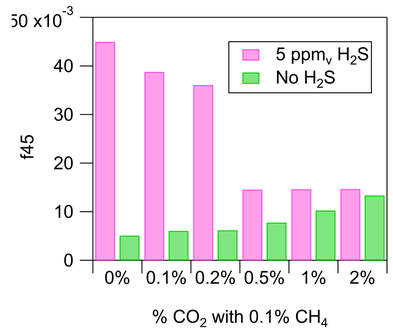
- Organic oxidized sulfur formed at all CO2 mixing ratios investigated and accounted for the majority of the sulfate formed for CO_2 < 1%



- Illustration of conclusions. The organic aerosol is independent of O:C/%CO_2 and inorganic and organic sulfur are produced with H_2S included.

CONCLUSIONS & SIGNIFICANCE

- Trace amounts of H_2S (5 ppmv) in Archean-like gas mixtures produced organic and sulfate aerosol, ***even at CO_2 : CH_4 ratios > ~1***.
- There was ***no evidence for S_8 or H_2SO_4*** found at any CO_2 mixing ratio studied here.
- We found evidence for both ***inorganic and organic sulfur*** aerosol, including ***organic oxidized sulfur*** and ***organic reduced sulfur*** (see figure below).



- These results ***differ from the current thought*** of Archean atmospheric sulfur reservoirs.[5,6]
- Potential implications for Archean sulfur isotopic records, the Archean atmosphere/climate, biological impacts such as early life and nutrient sources, and for CO_2/CH_4 haze chemistry in exoplanetary atmospheres.[7-10]

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