The influence of cloud droplet heterogeneity on in-cloud sulfate production

Becky Alexander

University of Washington

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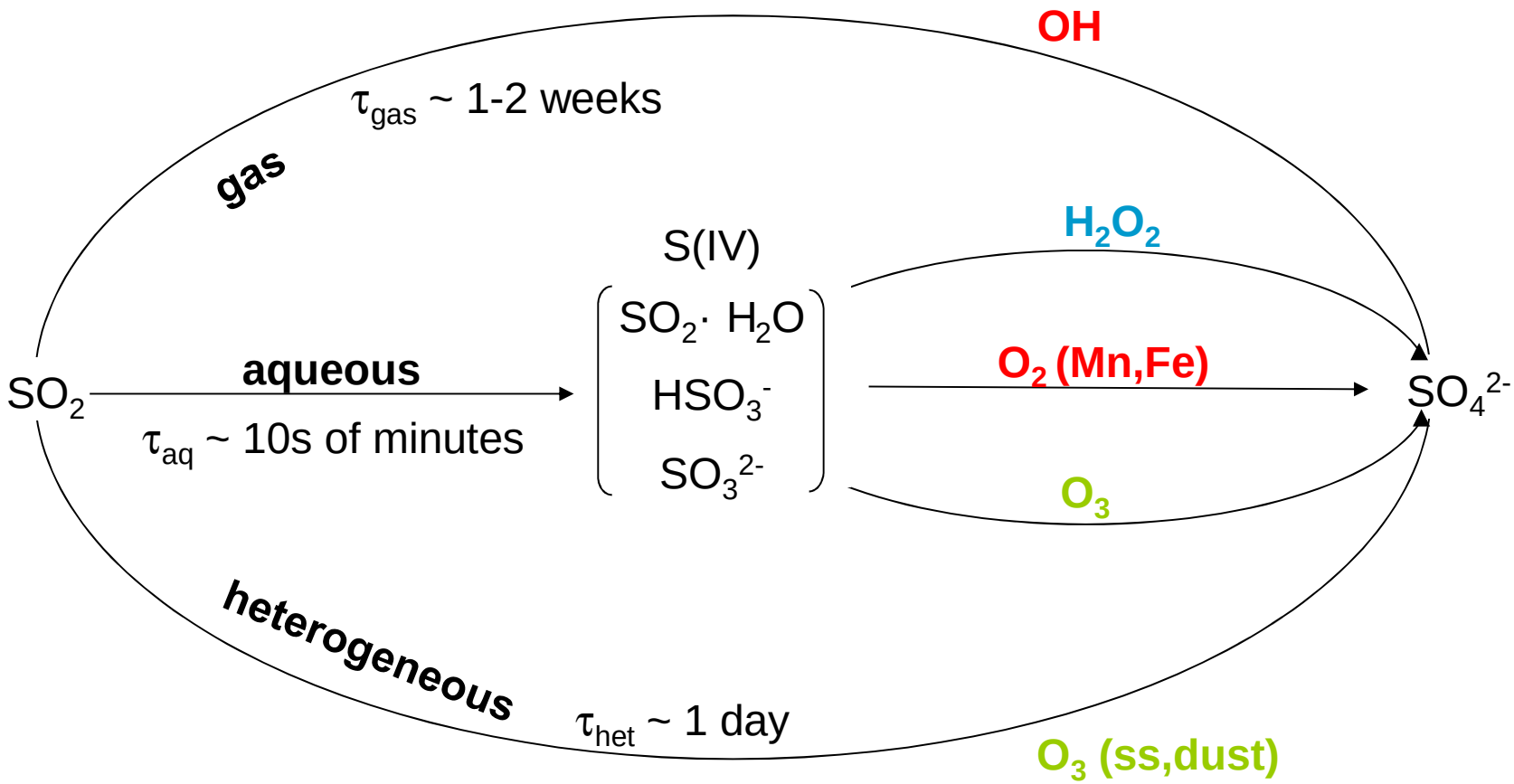
Sulfate Oxygen Isotopes

$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$



$\Delta^{17}O(SO_4^{2-})$ reflects the relative importance of each sulfate formation pathway to total sulfate abundance.

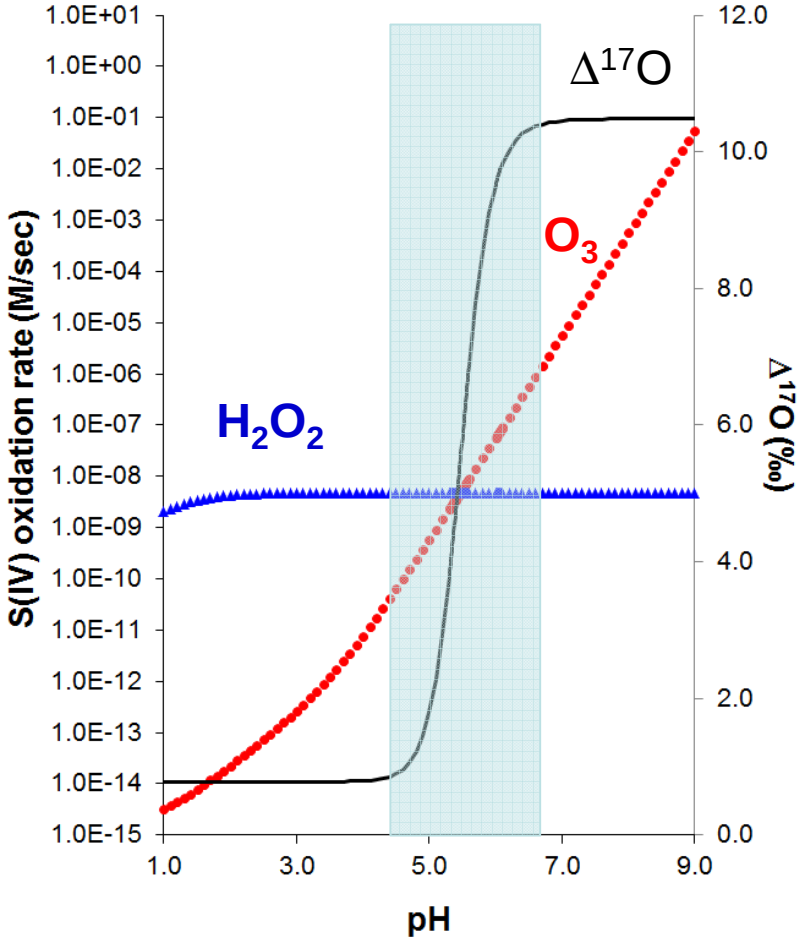
$\Delta^{17}O(SO_2) = 0‰$

$\Delta^{17}O(SO_4^{2-}) = 0‰$

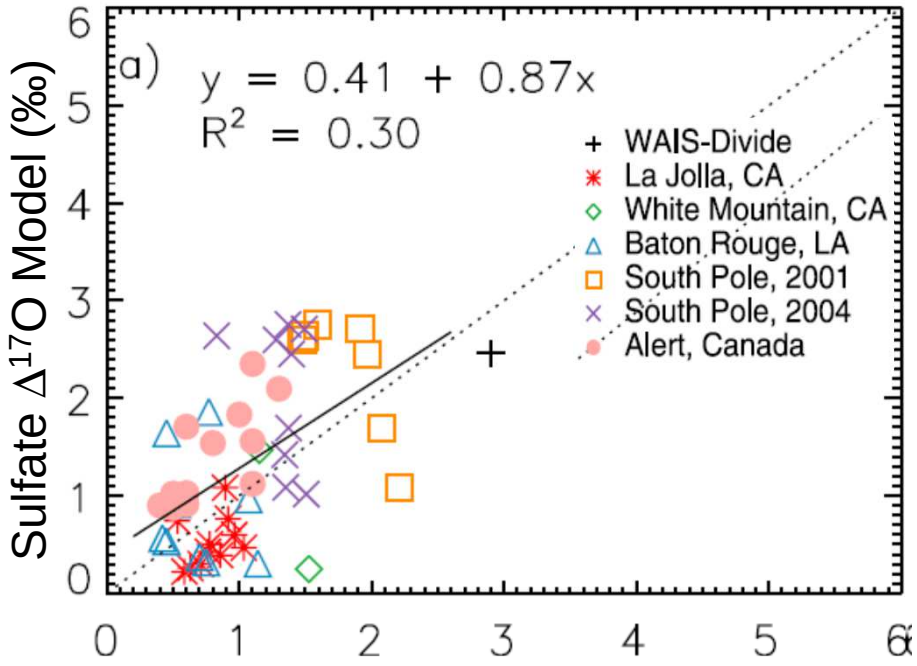
$\Delta^{17}O(SO_4^{2-}) = 1‰$

$\Delta^{17}O(SO_4^{2-}) = 9‰$

Influence of cloud pH on sulfate $\Delta^{17}O$



Cloud pH = 4.5 in GEOS-Chem



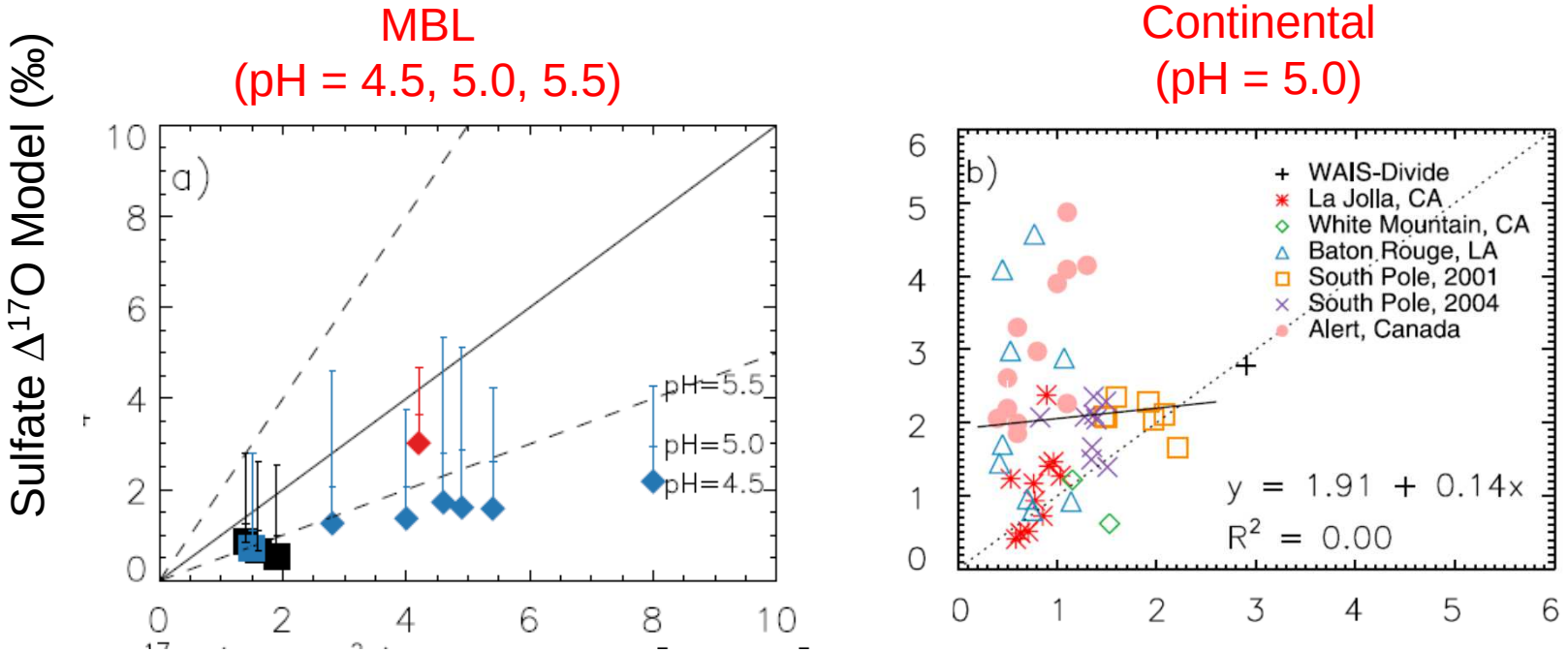
Sulfate $\Delta^{17}O$ is highly sensitive to pH (between pH ~4.5 - 6.5).

Good agreement between observed and modeled continental sulfate $\Delta^{17}O$ assuming pH = 4.5.

Model-observation comparison during the RODA campaign

MBL
(pH = 4.5, 5.0, 5.5)

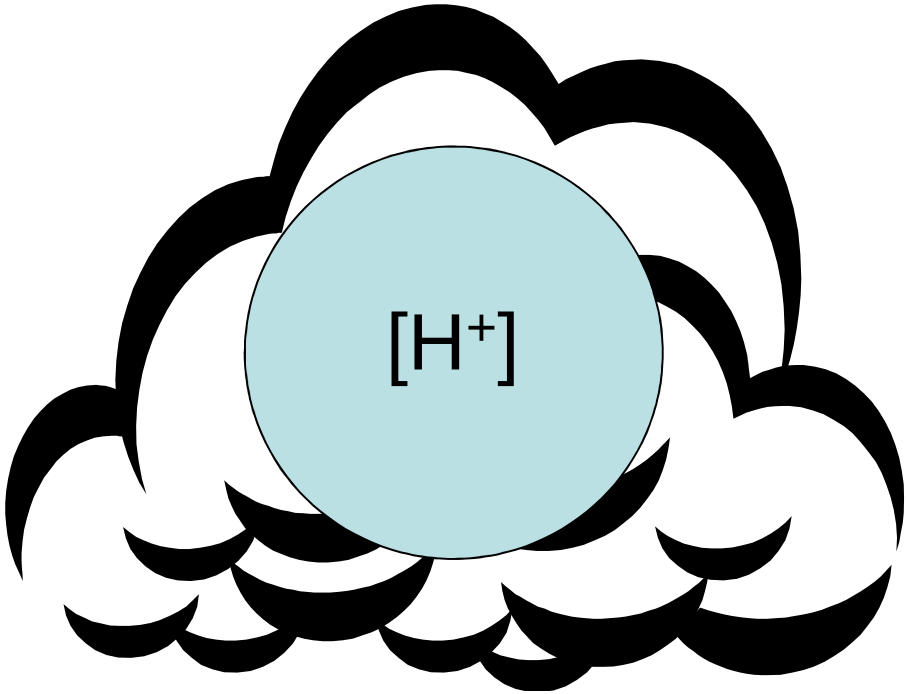
Continental
(pH = 5.0)



Modeled MBL Sulfate $\Delta^{17}O$ is too low. Increasing pH leads to poor agreement with continental observations.

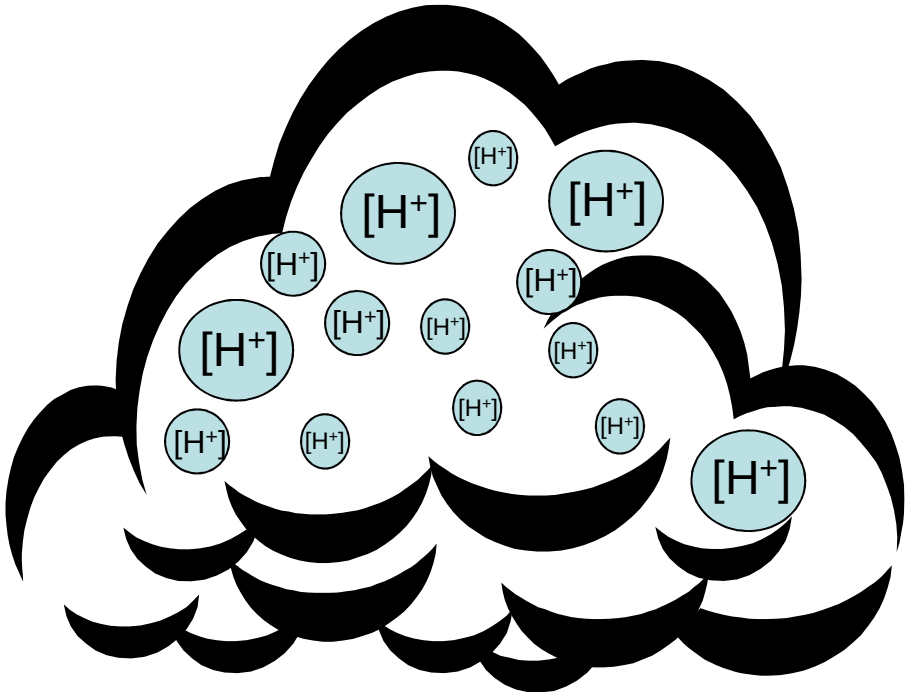
pH and cloud droplet heterogeneity

Bulk cloud pH assumption



Bulk pH underestimates the fraction of S(IV) that is SO_3^{2-}

Cloud drop heterogeneity



Smaller cloud droplets are more acidic

Modeled “bulk” cloud pH assumption underestimates sulfate production rates by underestimating the O_3 formation pathway

Accounting for cloud pH heterogeneity in a global model

[Yuen et al., 1996]

Bulk cloud pH calculation

SO_4^{2-}

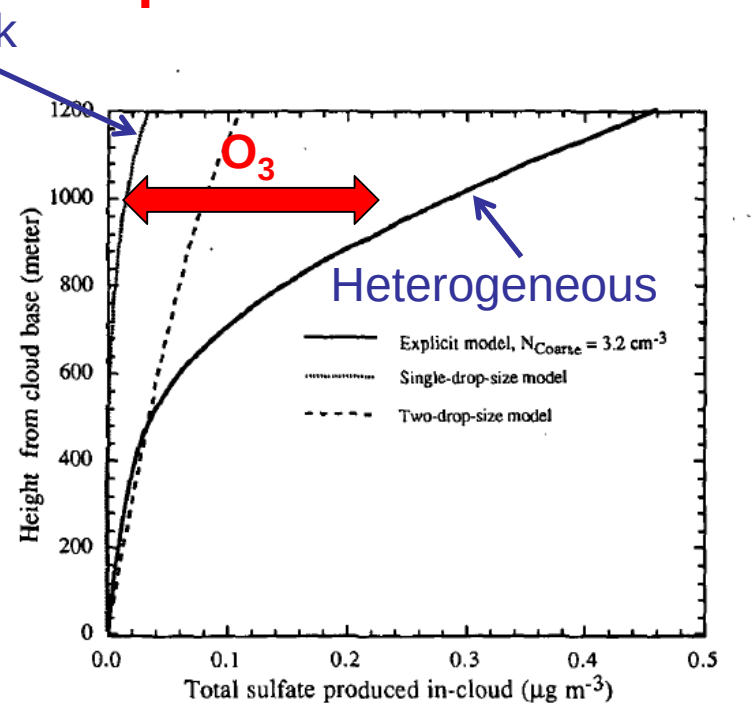
HCO_3^-, CO_3^{2-}

HSO_3^-, SO_3^{2-}

OH^-, H^+

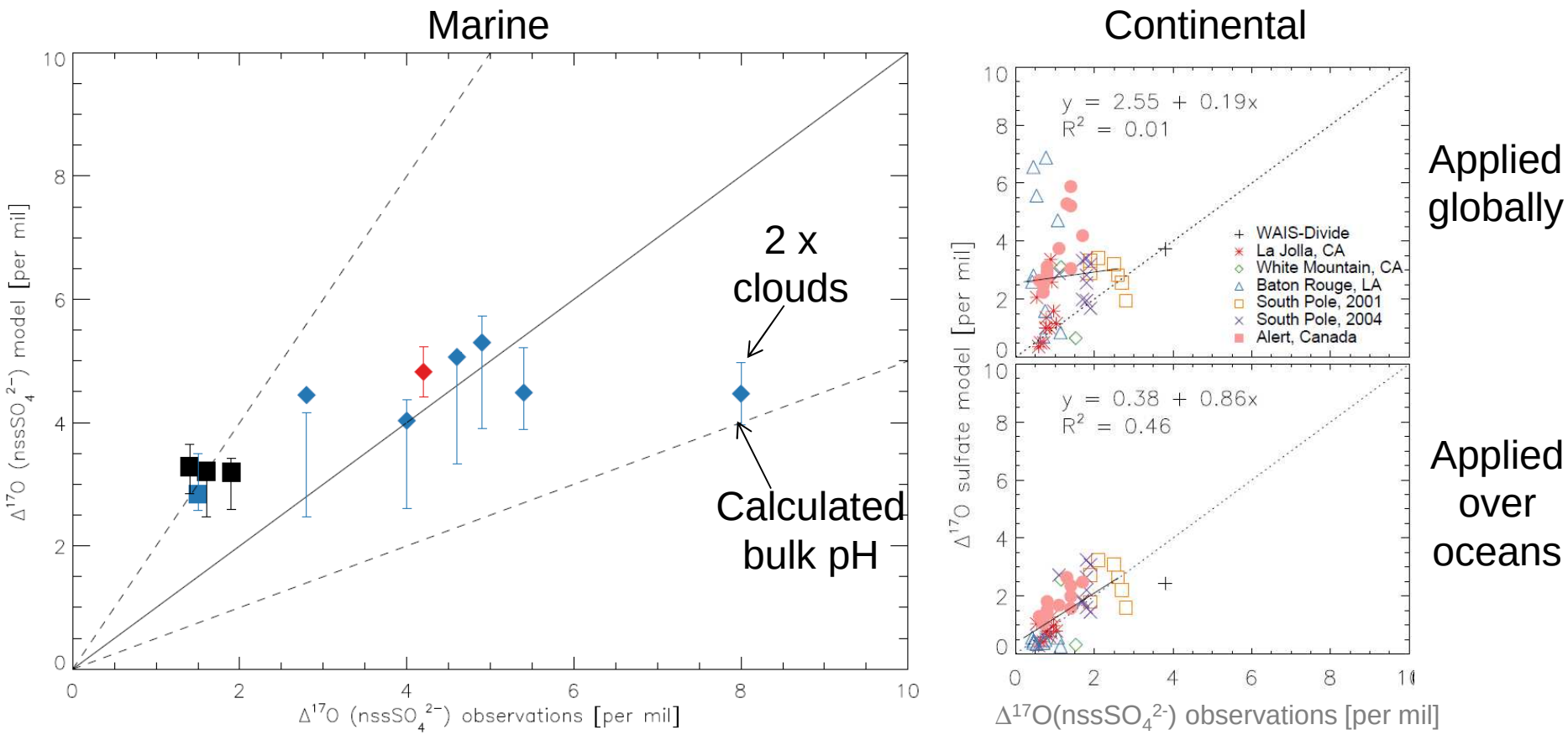
NH_4^+ NO_3^-

Cloud heterogeneity parameterization



Parameterization is a transfer function relating bulk and explicit model predictions of in-cloud sulfate formation based on a regression analysis.

Sulfate $\Delta^{17}O$ with heterogeneous cloud droplet pH



Applied globally

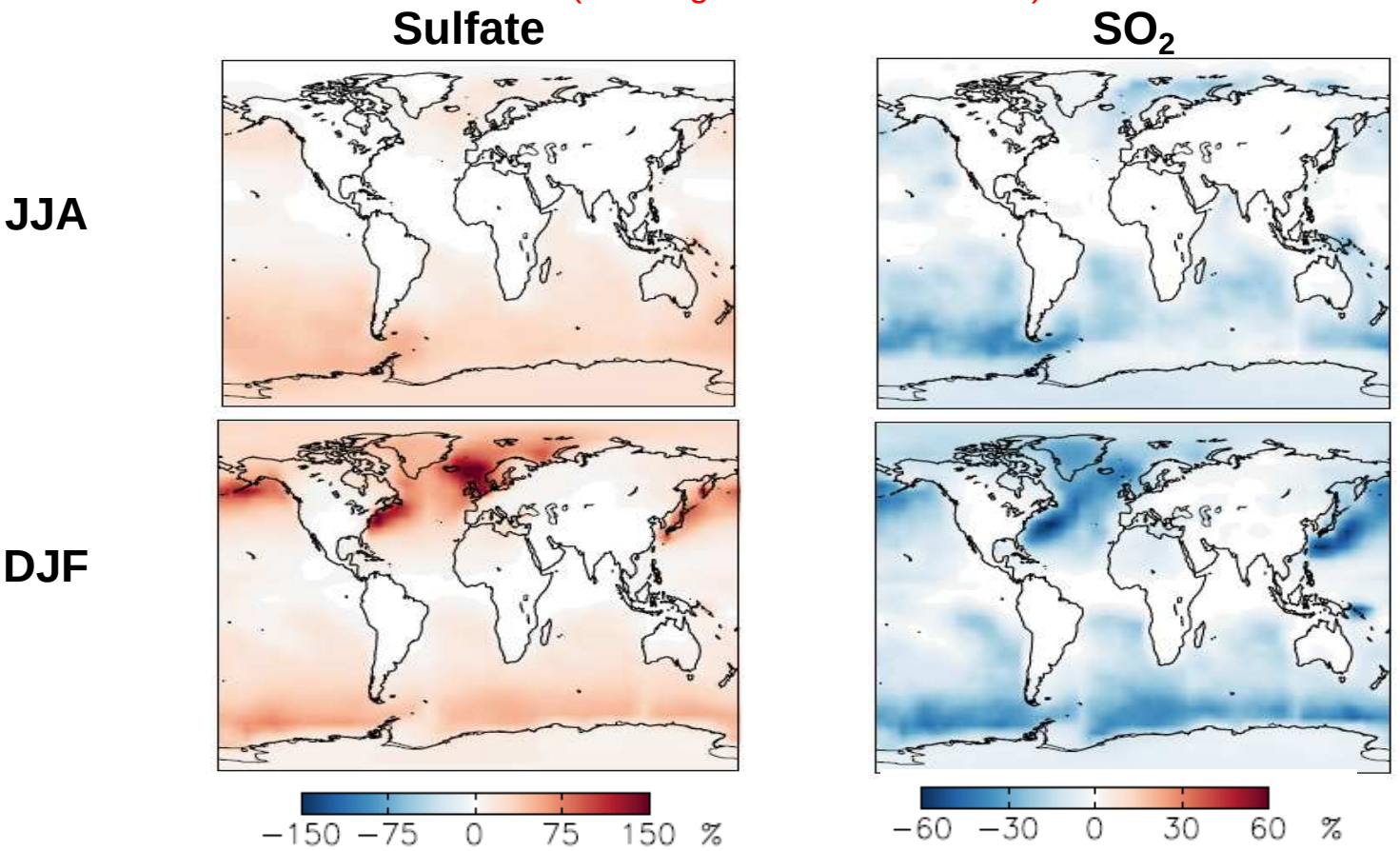
Applied over oceans

Yuen et al. parameterization applied over the oceans (not continents) provides best agreement with all observations.

Impacts of heterogeneous cloud pH on $[SO_4^{2-}]$ and $[SO_2]$ at the surface

% Change in Mass Concentration

(Heterogeneous – Bulk / Bulk) * 100



Heterogeneous cloud pH increases sulfate and decreases SO_2 concentrations over the oceans.

Conclusions and Future Directions

- Heterogeneous cloud pH increases in-cloud sulfate production and sulfate concentrations, and decreases aerosol pH over the oceans compared to bulk pH assumptions/calculations.
- More MBL and continental (especially inland) observations of $\Delta^{17}O(SO_4^{2-})_{nss}$ are needed to confirm results.
- Need to understand influence of dust (dissolved fraction) and organics on heterogeneous cloud pH and in-cloud sulfate production over continental regions.

For more details, please see *Alexander et al*., JGR, 2012.

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