Heterogeneous Sulfate Formation in Chinese Haze Events

Jingyuan Shao, Qianjie Chen, Pengzhen He, Zhouqing Xie, Yuxuan Wang, Lin Zhang, and Becky Alexander

Shao et al. [2019] (recently accepted to ACP)
Sulfate oxygen isotopes ($\Delta^{17}O$) depend on sulfate production mechanisms

\[ \Delta^{17}O(SO_4^{2-}) = 9.8\%o \quad \text{S(IV) + O}_3 \]

\[ \Delta^{17}O(SO_4^{2-}) = 0.7\%o \quad \text{S(IV) + H}_2\text{O}_2 \]

\[ \Delta^{17}O(SO_4^{2-}) = 0\%o \quad \text{Everything else*} \]

\*Everything else also includes primary anthropogenic sulfate
Observations of sulfate oxygen isotopes in Beijing

October 2014 – January 2015

Polluted days: PM$_{2.5} \geq$ 75 μg m$^{-3}$

$SOR = \frac{nSO_4^{2-}}{nSO_4^{2-} + nSO_2}$

Average $\Delta^{17}$O(SO$_4^{2-}$) = 0.9 ± 0.3‰

$S(IV) + O_3$: 2 – 9%
$S(IV) + H_2O_2$: 0 – 88%
All other pathways: 8 – 87%

He et al., ACP, 2018
Sulfate oxygen isotopes sensitive to aerosol pH

Calculated Heterogeneous Sulfate Production Rate and $\Delta^{17}$O(SO$_4^{2-}$)

Shao et al., ACP, 2019
Sulfate oxygen isotopes sensitive to aerosol pH

Calculated Heterogeneous Sulfate Production Rate and $\Delta^{17}$O(SO$_4^{2-}$)

Aerosol pH of 3.5 – 4.5 leads to $\Delta^{17}$O(SO$_4^{2-}$) = 0.7‰

Shao et al., ACP, 2019
Sulfate oxygen isotopes sensitive to aerosol pH

Calculated Heterogeneous Sulfate Production Rate and $\Delta^{17}\text{O}(\text{SO}_4^{2-})$

Aerosol pH of 5.5 – 6.5 leads to $\Delta^{17}\text{O}(\text{SO}_4^{2-}) = 1 - 6\%$.
Meteorology from GEOS-FP from observation period: October 2014 – January 2015

- 1/4° x 5/16° horizontal resolution, 15 minute chemical time step, 47 vertical layers
- ISORROPIA II thermodynamic model [Fountoukis and Nenes, 2007] for aerosol pH

Heterogeneous sulfate production added to the model

\[ \begin{align*}
  &\text{gas} \\
  S(\text{IV}) &\rightarrow \begin{cases}
    \text{SO}_2 \cdot \text{H}_2\text{O} \\
    \text{HSO}_3^- \\
    \text{SO}_3^{2-}
  \end{cases} \\
  &\text{aqueous} \\
  \text{SO}_2 &\rightarrow \begin{cases}
    \tau_{\text{aq}} \sim 10\text{s of minutes} \\
    \tau_{\text{het}} \sim 1\text{ day}
  \end{cases} \\
  &\text{heterogeneous} \\
  \text{OH} &\rightarrow \begin{cases}
    \text{H}_2\text{O}_2 \\
    \text{O}_3 \\
    \text{O}_2 \text{ (Mn,Fe)} \\
    \text{NO}_2
  \end{cases}
Modeled Sulfate Concentration and Formation

Sulfate dominated by gas-phase oxidation by OH and in-cloud oxidation by TMI in polluted conditions, primary sulfate in clean conditions.
Modeled Sulfate Concentration and Formation

Gas and in-cloud only

Model underestimates \( \Delta^{17}O(SO_4^{2-}) \), suggesting an underestimate of O\(_3\) oxidation.
Heterogeneous sulfate formation ~20%, dominated by TMI.
Model underestimates observed $\Delta^{17}$O(SO$_4^{2-}$), but less so than without het. chem.
Modeled Sulfate Concentration and Formation

$\text{SOR} = \frac{nSO_4^{2-}}{nSO_4^{2-} + nSO_2}$

Model underestimates PM$_{2.5}$ (-25%), sulfate (-40%), and SOR (-28%) during polluted periods.
Sulfate production on externally-mixed alkaline dust aerosol may represent up to ~10% of sulfate production in Beijing [Fairlie et al., 2010], which would increase the modeled $\Delta^{17}$O(SO$_4^{2-}$) similar to observations.
Conclusions

• Calculations suggest ~20% of sulfate abundance originates from heterogeneous chemistry, with metal-catalyzed oxidation dominating. The importance of TMI is uncertain due to uncertainties in abundance of dissolved concentrations of Mn(II) and Fe(III).

• Sulfate production on the order of 10% of total sulfate abundance on externally-mixed alkaline dust aerosol would increase the modeled $\Delta^{17}O\left(\text{SO}_4^{2-}\right)$ similar to observations but cannot reconcile the model’s low bias in sulfate concentrations and SOR.

• Observed $\Delta^{17}O\left(\text{SO}_4^{2-}\right)$ is consistent with a negligible role for NO$_2$ oxidation, (up to a few % of total sulfate formation).