

1 **Table S1.** Reaction rate expression and constant for SO₂ oxidation by OH in the gas-phase.

Oxidant	The reaction rate expression and constant ^a	References
OH	$R_{\text{SO}_2+\text{OH}} = k_0[\text{SO}_2(\text{g})][\text{OH}(\text{g})]$ $k_{0\text{low}} = 3.3 \times 10^{-31} \times (T/300)^{-4.3} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_{0\text{high}} = 1.6 \times 10^{-12} \times (T/300)^0 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_c = 0.6$	(Burkholder et al., 2015)

2 ^a We report the low and high pressure limit of k for SO₂ oxidation by OH. F_c is used to calculate the dependence of k on
3 pressure and temperature (details see the reference (Burkholder et al., 2015)).

4 **Table S2.** The daytime average OH concentration.

Cases ^a	Daytime OH concentration ($\times 10^6 \text{ molecule cm}^{-3}$) ^b	References
PD of Case I and II	3.5	(Rao et al., 2016)
NPD of Case I and II	4.9	
PD of Case III to V	0.34	
NPD of Case III to V	0.99	

5 ^a PD refers to polluted days ($\text{PM}_{2.5} \geq 75 \mu\text{g m}^{-3}$), NPD refers to non-polluted days ($\text{PM}_{2.5} < 75 \mu\text{g m}^{-3}$).

6 ^b The daytime (08:00–20:00 LT) OH concentration in PD of Case I and II in October 2014 was taken from the value reported
7 in summer haze in Beijing, and the daytime OH concentration in NPD of Case I and II was taken from the value reported in
8 summer non-haze in Beijing (Rao et al., 2016). The daytime OH concentration in PD of Case III to V in November 2014 to
9 January 2015 was taken from the value reported in winter haze in Beijing, and the daytime OH concentration in NPD of
10 Case III to V was taken from the value reported in winter non-haze in Beijing (Rao et al., 2016).

11 **Table S3.** Aqueous-phase reaction rate expressions, rate constants (k) and influence of ionic strength (I_s) on k for sulfate
12 production in aerosol and cloud water.

Oxidants	The reaction rate expressions ($R_{\text{S(IV)+oxi}}$), constants (k) and influence of I_s (in unit of M) on k ^a	Notes	References
O ₃	$(k_1[\text{H}_2\text{SO}_3] + k_2[\text{HSO}_3^-] + k_3[\text{SO}_3^{2-}]][\text{O}_3(\text{aq})]$ $k_1 = 2.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ $k_2 = 3.7 \times 10^5 \times e^{(-5530 \times (1/T-1/298))} \text{ M}^{-1} \text{ s}^{-1}$ $k_3 = 1.5 \times 10^9 \times e^{(-5280 \times (1/T-1/298))} \text{ M}^{-1} \text{ s}^{-1}$ $\log_{10}\left(\frac{k}{k_{I_s=0}}\right) = b_1 \left(\frac{\sqrt{I_s}}{1+\sqrt{I_s}} - 0.3I_s\right)$ b_1 is in range of 0.7 to 1.3 ^b $\frac{k}{k_{I_s=0}} = 1 + b_2 I_s$	$I_{s, \text{max}} = 0.94 \text{ M}$ $I_{s, \text{max}} = 1.2 \text{ M}$	(Hoffmann and Calvert, 1985) (Maahs, 1983) (Lagrange et al., 1994)

	b_2 is in range of 0.8 to 3.7 ^b		
H ₂ O ₂	$k_4[\text{H}^+][\text{HSO}_3^-][\text{H}_2\text{O}_2(\text{aq})]/(1+K[\text{H}^+])$ $k_4 = 7.45 \times 10^7 \times e^{(-4430 \times (1/T-1/298))} \text{ M}^{-1} \text{ s}^{-1}$ $K = 13 \text{ M}^{-1}$	(McArdle and Hoffmann, 1983)	
	$\log_{10}\left(\frac{k}{k^{I_s=0}}\right) = 0.36I_s - \frac{1.018\sqrt{I_s}}{1+0.17\sqrt{I_s}}$	$I_{s, \max} = 5 \text{ M}$	(Maaß et al., 1999)
NO ₂	$k_5[\text{S(IV)}][\text{NO}_2(\text{aq})]^c$ $k_{5\text{low}} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ $k_{5\text{high}} = (1.24-2.95) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	(Clifton et al., 1988; Lee and Schwartz, 1982)	
	$\log_{10}\left(\frac{k}{k^{I_s=0}}\right) = b_3I_s$ $b_3 > 0^d$	Theoretical prediction	(Cheng et al., 2016)
O ₂ ^e	$k_6[\text{H}^+]^{-0.74}[\text{S(IV)}][\text{Mn(II)}][\text{Fe(III)}]$ (pH ≤ 4.2) $k_6 = 3.72 \times 10^7 \times e^{(-8431.6 \times (1/T-1/297))} \text{ M}^{-2} \text{ s}^{-1}$ $k_7[\text{H}^+]^{0.67}[\text{S(IV)}][\text{Mn(II)}][\text{Fe(III)}]$ (pH > 4.2) $k_7 = 2.51 \times 10^{13} \times e^{(-8431.6 \times (1/T-1/297))} \text{ M}^{-2} \text{ s}^{-1}$	(Ibusuki and Takeuchi, 1987)	
	$\log_{10}\left(\frac{k}{k^{I_s=0}}\right) = \frac{b_4\sqrt{I_s}}{1+\sqrt{I_s}}$ b_4 is in range of -4 to -2	$I_{s, \max} = 2 \text{ M}$	(Martin and Hill, 1967; Martin et al., 1991)
	$k_8 = 1.5 \times 10^6 [\text{S(IV)}] (\text{M s}^{-1}, \text{pH} \leq 3, \text{microdroplets})^f$		(Hung and Hoffmann, 2015)

13 ^a The influence of I_s was not considered for in-cloud calculation due to the estimated I_s of cloud water being negligible
14 (around $3 \times 10^{-3} \text{ M}$) in North China Plain (NCP) (Guo et al., 2012; Wang et al., 2011). The cloud pH was set to be 4.6 in the
15 present study, which is the mean value observed in NCP with typical range of 3–5 (Guo et al., 2012; Shen et al., 2012; Wang
16 et al., 2011).

17 ^b The values of b_1 and b_2 are different for different solutions (Maahs, 1983; Lagrange et al., 1994). Since these values vary
18 largely and have a significant impact on the estimated reaction rate at high I_s in aerosol water, the relative importance of
19 heterogeneous sulfate production via S(IV) + O₃ in aerosol water was not estimated by chemical reaction kinetics calculation
20 but estimated with the constraint of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$.

21 ^c The $k_{5\text{low}}$ was taken from Lee and Schwartz (1982). They reported a lower-limit value of $k_{5\text{low}} = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH of 5.8
22 and 6.4. The $k_{5\text{high}}$ is in the pH range of 5.3–13 as reported by Clifton et al. (1988) and it increases with increasing pH. We
23 used the value $k_{5\text{high}} = 1.24 \times 10^7$ for pH < 5.3, and $k_{5\text{high}} = (0.1239 \times \text{pH} + 0.5954) \times 10^7$ derived from Clifton et al. (1988) for pH
24 in 5.3–7.8 in this study.

25 ^d The b_3 was predicted theoretically to be positive (Cheng et al., 2016), however, no specific value of b_3 was determined
26 from laboratory work. Thus we didn't consider the influence of I_s on S(IV) + NO₂ in aerosol water in our calculation, which
27 is consistent with Cheng et al. (2016).

28 ^e S(IV) oxidation by O₂, which is via a radical chain mechanism, can be initiated by transition metal ions (TMIs) in bulk
 29 water (k_6 and k_7) or initiated due to the speciality of interfacial water on acidic microdroplets (k_8). Thus in our calculation,
 30 the reaction rate k_6 and k_7 was used for in-cloud sulfate production via S(IV) + O₂, while k_8 was used for heterogeneous
 31 sulfate production.

32 ^f This mechanism is not well studied so far, i.e., the influence of I_s on k_8 remains unknown, and the value of k_8 is not reported
 33 when pH is > 3 even though it decreases with increasing pH when pH is > 3 (Hung and Hoffmann, 2015). To be not
 34 speculative, this mechanism was used at pH = 3 with I_s being not considered.

35 **Table S4.** The input and output of ISORROPIA II model.

	Non-polluted days		Polluted days		Total	
	mean	range	mean	range	mean	range
Observed inorganic ion concentrations ($\mu\text{g m}^{-3}$)						
SO ₄ ²⁻	3.9±1.8	1.5–6.6	28.4±12.5	8.2–56.4	21.2±15.4	1.5–56.4
NO ₃ ⁻	6.1±5.3	0.3–14.8	48.4±24.7	7.7–106.7	35.9±28.5	0.3–106.7
NH ₄ ⁺	3.6±3.8	0.0–10.0	28.6±8.7	11.0–43.0	21.3±13.8	0.0–43.0
Cl ⁻	1.5±1.8	0.0–5.3	5.5±4.1	0.5–15.0	4.3±4.0	0.0–15.0
K ⁺	1.5±1.7	0.1–5.9	2.9±1.2	1.5–7.3	2.5±1.5	0.1–7.3
Na ⁺	0.2±0.2	0.0–0.5	0.7±0.2	0.4–1.2	0.6±0.3	0.0–1.2
Ca ²⁺	3.3±2.0	0.5–6.2	1.3±1.1	0.0–4.7	1.9±1.7	0.0–6.2
Mg ²⁺	0.2±0.1	0.0–0.4	0.2±0.1	0.0–0.6	0.2±0.1	0.0–0.6
Calculated NH ₃ (ppb)	6.9±3.3	2.1–10.7	13.1±3.1	5.7–18.0	11.3±4.2	2.1–18.0
Observed meteorological parameters ^a						
Temperature (T , °C)	2.6±6.2	–4.5–11.1	6.8±6.9	–4.3–17.7	5.6±6.9	–4.5–17.7
Relative humidity (RH, %)	37±12	21–58	62±12	35–80	54±17	21–80
Modelled aerosol parameters						
Stable mode						
Aerosol water content (AWC, $\mu\text{g m}^{-3}$)	5.3±7.4	0.0–16.3	63.5±54.6	0.9–196.1	54.6±54.5	0.0–196.1
Aerosol pH	7.5±0.1	7.5–7.6	7.6±0.1	7.5–7.8	7.6±0.1	7.5–7.8
I_s (M)	26.5±9.5	17.5–36.4	27.6±12.2	11.3–51.6	27.4±11.8	11.3–51.6
Metastable mode						
AWC ($\mu\text{g m}^{-3}$)	9.6±6.0	2.6–16.3	84.2±49.2	9.2–198.1	72.7±52.8	2.6–198.1
Aerosol pH	6.5±1.3	4.9–7.6	4.4±0.6	3.4–5.4	4.7±1.1	3.4–7.6
I_s (M)	29.3±11.2	17.5–44.1	26.4±10.6	11.4–46.1	26.8±10.5	11.4–46.1

44 ^b Different salt solutions were found to have different effects on $H_{H_2O_2}$, the reported relationships between $H_{H_2O_2}$ and
 45 different salts ($(NH_4)_2SO_4$, NH_4NO_3 and NH_4Cl) were measured at 292K (Chung et al., 2005). In the mixture of salt
 46 solutions, $H_{H_2O_2}$ can be estimated as: $H(\text{mixture}) = H^{I_s=0} + (H(\text{Salt 1}) - H^{I_s=0}) + (H(\text{Salt 2}) - H^{I_s=0}) + (H(\text{Salt 3}) - H^{I_s=0})$ (Chung et
 47 al., 2005).

48 ^c We didn't consider the influence of I_s on H_{NO_2} in our calculation due to the lack of relevant laboratory data.

49 **Table S6.** Observed $\Delta^{17}O(SO_4^{2-})$ in aerosols or rainwater in mid-latitude areas.

$\Delta^{17}O(SO_4^{2-})$ range (‰)	Sample	Locations	Time	References
0.1–1.6 (0.9±0.3)	Aerosol	Beijing, China	October 2014 to January 2015	This study
0.47–1.50 (0.92)	Aerosol	La Jolla, USA	February 2009 to August 2010	(Hill - Falkenthal et al., 2012)
1.19–3.00	Aerosol	Bakersfield, USA	December 1998 to January 1999	(Romero and Thiemens, 2003)
1.0–1.6	Aerosol	Mount Barcroft, USA	August 1996 to March 1997	(Lee and Thiemens, 2001)
0.2–1.6	Aerosol	La Jolla, USA	May 1996 to December 1997	(Lee and Thiemens, 2001)
0.14–1.02 (0.53±0.19)	Rainwater	Wuhan, China	April 2009 to September 2011	(Li et al., 2013)
0.26–1.43 (0.62±0.32)	Rainwater	Baton Rouge, USA	August 2003 to March 2005	(Jenkins and Bao, 2006)
0.2–1.4	Rainwater	La Jolla, USA	November 1997 to February 1998	(Lee and Thiemens, 2001)
0.02–4.23 (1.0±0.6)	Aerosol, dust, rainwater	Southwestern USA	November 1998 to April 1999	(Bao and Reheis, 2003)
0.80–1.62 (1.30)	Snowpack	The Rocky Mountains, USA	1994 to 2000	(Johnson et al., 2001)

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51 References

52 Bian, Y., Zhao, C., Ma, N., Chen, J., and Xu, W.: A study of aerosol liquid water content based on hygroscopicity
 53 measurements at high relative humidity in the North China Plain, *Atmos. Chem. Phys.*, 14, 6417-6426, 2014.

54 Burkholder, J., Sander, S., Abbatt, J., Barker, J., Huie, R., Kolb, C., Kurylo, M., Orkin, V., Wilmouth, D., and Wine, P.:
55 Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 18, Pasadena, CA: Jet
56 Propulsion Laboratory, National Aeronautics and Space Administration, 2015, 2015.

57 Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., and Carmichael, G.: Reactive
58 nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, *Sci. Adv.*, 2, e1601530, 2016.

59 Chung, M., Muthana, S., Paluyo, R., and Hasson, A.: Measurements of effective Henry's law constants for hydrogen
60 peroxide in concentrated salt solutions, *Atmos. Environ.*, 39, 2981-2989, 2005.

61 Clifton, C. L., Altstein, N., and Huie, R. E.: Rate constant for the reaction of nitrogen dioxide with sulfur (IV) over the pH
62 range 5.3-13, *Environ. Sci. Technol.*, 22, 586-589, 1988.

63 Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett, J. L., and Wang, W.: Characterization of
64 cloud water chemistry at Mount Tai, China: Seasonal variation, anthropogenic impact, and cloud processing, *Atmos.*
65 *Environ.*, 60, 467-476, 2012.

66 Hoffmann, M. R., and Calvert, J. G.: Chemical Transformation Modules for Eulerian Acid Deposition Models: Volume II,
67 the Aqueous-phase Chemistry, Atmospheric Sciences Research Laboratory, Office of Research and Development, US
68 Environmental Protection Agency, 1985.

69 Hung, H.-M., and Hoffmann, M. R.: Oxidation of gas-Phase SO₂ on the surfaces of acidic microdroplets: Implications for
70 sulfate and sulfate radical anion formation in the atmospheric liquid phase, *Environ. Sci. Technol.*, 49, 13768-13776,
71 2015.

72 Ibusuki, T., and Takeuchi, K.: Sulfur dioxide oxidation by oxygen catalyzed by mixtures of manganese (II) and iron (III) in
73 aqueous solutions at environmental reaction conditions, *Atmos. Environ.*, 21, 1555-1560, 1987.

74 Kosak-Channing, L. F., and Helz, G. R.: Solubility of ozone in aqueous solutions of 0-0.6 M ionic strength at 5-30. degree.
75 C, *Environ. Sci. Technol.*, 17, 145-149, 1983.

76 Lagrange, J., Pallares, C., and Lagrange, P.: Electrolyte effects on aqueous atmospheric oxidation of sulphur dioxide by
77 ozone, *J. Geophys. Res.*, 99, 14595-14600, 1994.

78 Lee, Y. N., and Schwartz, S. E.: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, in: Kinetics of oxidation of
79 aqueous sulfur (IV) by nitrogen dioxide, Precipitation scavenging, dry Deposition and resuspension, California, 1982,
80 453-470, 1983.

81 Maaß, F., Elias, H., and Wannowius, K. J.: Kinetics of the oxidation of hydrogen sulfite by hydrogen peroxide in aqueous
82 solution:: ionic strength effects and temperature dependence, *Atmos. Environ.*, 33, 4413-4419, 1999.

83 Maahs, H. G.: Kinetics and mechanism of the oxidation of S (IV) by ozone in aqueous solution with particular reference to
84 SO₂ conversion in nonurban tropospheric clouds, *J. Geophys. Res.*, 88, 10721-10732, 1983.

85 Martin, L., Hill, M., Tai, A., and Good, T.: The iron catalyzed oxidation of sulfur (IV) in aqueous solution: differing effects
86 of organics at high and low pH, *J. Geophys. Res.*, 96, 3085-3097, 1991.

87 Martin, L. R., and Hill, M. W.: The iron catalyzed oxidation of sulfur: Reconciliation of the literature rates, *Atmos. Environ.*,
88 21, 1487-1490, 1967.

89 McArdle, J. V., and Hoffmann, M. R.: Kinetics and mechanism of the oxidation of aquated sulfur dioxide by hydrogen
90 peroxide at low pH, *J. Phys. Chem.*, 87, 5425-5429, 1983.

91 Millero, F. J., Hershey, J. B., Johnson, G., and Zhang, J.-Z.: The solubility of SO₂ and the dissociation of H₂SO₃ in NaCl
92 solutions, *J. Atmos. Chem.*, 8, 377-389, 1989.

93 Rao, Z., Chen, Z., Liang, H., Huang, L., and Huang, D.: Carbonyl compounds over urban Beijing: Concentrations on haze
94 and non-haze days and effects on radical chemistry, *Atmos. Environ.*, 124, 207-216, 2016.

95 Seinfeld, J. H., and Pandis, S. N.: *Atmospheric chemistry and physics: From air pollution to climate change*, John Wiley &
96 Sons, New Jersey, 2012.

97 Shen, X., Lee, T., Guo, J., Wang, X., Li, P., Xu, P., Wang, Y., Ren, Y., Wang, W., and Wang, T.: Aqueous phase sulfate
98 production in clouds in eastern China, *Atmos. Environ.*, 62, 502-511, 2012.

99 Wang, Y., Guo, J., Wang, T., Ding, A., Gao, J., Zhou, Y., Collett, J. L., and Wang, W.: Influence of regional pollution and
100 sandstorms on the chemical composition of cloud/fog at the summit of Mt. Taishan in northern China, *Atmos. Res.*, 99,
101 434-442, 2011.

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