

## Supporting Information:

# OH-Radical Specific Addition to Glutathione S-Atom at the Air-Water Interface – Relevance to the Redox Balance of the Lung Epithelial Lining Fluid

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## SI Text

Ozone is produced from ultrapure O<sub>2</sub> (purity > 99.995 %) flowing at 1.0 standard liters per minute (SLM) through a discharge ozonizer (KSQ-050, Kotohira). O<sub>3</sub>(g) concentration is measured online by a UV-Vis absorption spectrophotometry at 300 nm (absorption cross section =  $3.9 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ ),<sup>1</sup> prior to entering the reaction chamber. Throughout, the reported [O<sub>3</sub>(g)] values correspond to the concentrations actually sensed by the microjets in the reaction chamber, which are 10 times smaller than those determined upstream UV absorbances due to dilution by the drying gas (N<sub>2</sub>). H<sub>2</sub>O(g) is constantly added by sparging milli-Q water with N<sub>2</sub>(g) carrier gas at 0.2 SLM, whose flow is measured by a mass flow controller. It is assumed that the chamber is saturated with H<sub>2</sub>O(g) at 298 K throughout. The 266 nm radiation emitted by our Nd<sup>3+</sup>:YAG laser setup (LOTIS TII, LS-2131M-10) through the harmonic generator assembly HG-TF (pulse duration  $8 \pm 1 \text{ ns}$ , 266 nm beam diameter  $10.0 \pm 1.0 \text{ mm}$ , beam divergence  $\leq 1.5 \text{ mrad}$ , 10 Hz) is used to generate ·OH(g) *in situ* (Fig. S1).

Conditions in the present experiments were: drying gas flow rate: 12 L min<sup>-1</sup>; drying gas temperature: 340 °C; inlet voltage: + 3.5 kV relative to ground; fragmentor voltage value: 60 V. GSH (> 97 %) and GSSG (> 98 %) were purchased from Tokyo Chemical Industry (Tokyo). Fe(II)Cl<sub>2</sub>·4H<sub>2</sub>O (> 99 %) was purchased from Sigma-Aldrich. All solutions were prepared in purified water (Resistivity  $\geq 18.2 \text{ M}\Omega \text{ cm}$  at 298 K) from a Millipore Milli-Q water purification system. These samples are acidic (pH 3-6) and used as they are without adjusting by NaOH. The pH of the injected solutions was measured before measurement with a calibrated pH-meter, Horiba LAQUA F-74.

## [·OH(g)] estimates

The photo-dissociation of  $O_3(g)$  by 266 nm into  $O(^1D)$ , followed by the reaction of  $O(^1D)$  with  $H_2O(g)$ , in competition with its quenching by  $N_2(g)$  and  $O_2(g)$  into  $O(^3P)$  promptly yields  $\cdot OH(g)$ .<sup>2</sup> The concentration of  $\cdot OH(g)$  is estimated from the  $O_3(g)$  absorption cross sections, laser fluence, and reported gas-phase kinetic parameters. Since number of photons is larger than number of  $O_3(g)$  molecules under present conditions, we could estimate the initial  $O(^1D)$  concentrations from 266 nm photolysis from Beer's law:

$$\ln(N_0/N) = I_0 \sigma \Phi_{dis} \quad (E 1)$$

$$N = N_0 \exp(-I_0 \sigma \Phi_{dis}) \quad (E 2)$$

where  $\sigma$  is the absorption cross section,  $\Phi_{dis}$  is the dissociation quantum yield,  $I_0$  is the laser fluence in number of photons per unit area,  $N_0$  is the number of molecules before laser irradiation, and  $N$  is the number of molecules after laser irradiation.<sup>3</sup>  $O(^1D)$  reacts with excess  $H_2O(g)$  ( $[H_2O(g)] \sim 7.6 \times 10^{17} \text{ molecule cm}^{-3}$ ) to generate  $\cdot OH$  radical within  $\sim 6$  ns (derived from  $k_1 = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), reaction R 1<sup>1,4</sup>;



or, is competitively quenched by  $N_2$  and  $O_2$ , reactions R 2a and R 2b<sup>1,4</sup>



We evaluate that  $\sim 20\%$   $O(^1D)$  is converted into  $\cdot OH$  radicals under present conditions. By changing  $[O_3(g)]$  and 266 nm laser energy,  $[\cdot OH]_0$  can be varied from a few tens of ppbv to 100 ppmv under present conditions.

The secondary chemistry by the reaction of  $\cdot OH$  with  $O_3$  ( $k = 7.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>4</sup> is unimportant since the  $\cdot OH$  lifetime by this reaction  $> 500 \mu\text{s}$ . It is also noted that the reaction of  $O(^1D)$  with reactant(aq) is negligible. By assuming a rate constant for

such process as large as  $k = 6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,<sup>5</sup> we estimate that this  $\text{O}(^1\text{D})$  reaction path at  $[\text{reactant}(\text{aq})] = 100 \text{ } \mu\text{M} = 6.0 \times 10^{16} \text{ molecules cm}^{-3}$ , is still > 20 times slower than the gas phase reactions R1, 2a and 2b. The fact that the same products were observed on aqueous GSH microjets 0.01 - 100 mM range also supports it. We also note that  $\text{O}(^3\text{P})$  is mainly consumed by  $\text{O}_2$  to regenerate  $\text{O}_3$  ( $\tau \sim 36 \text{ } \mu\text{s}$ ) under the present condition.

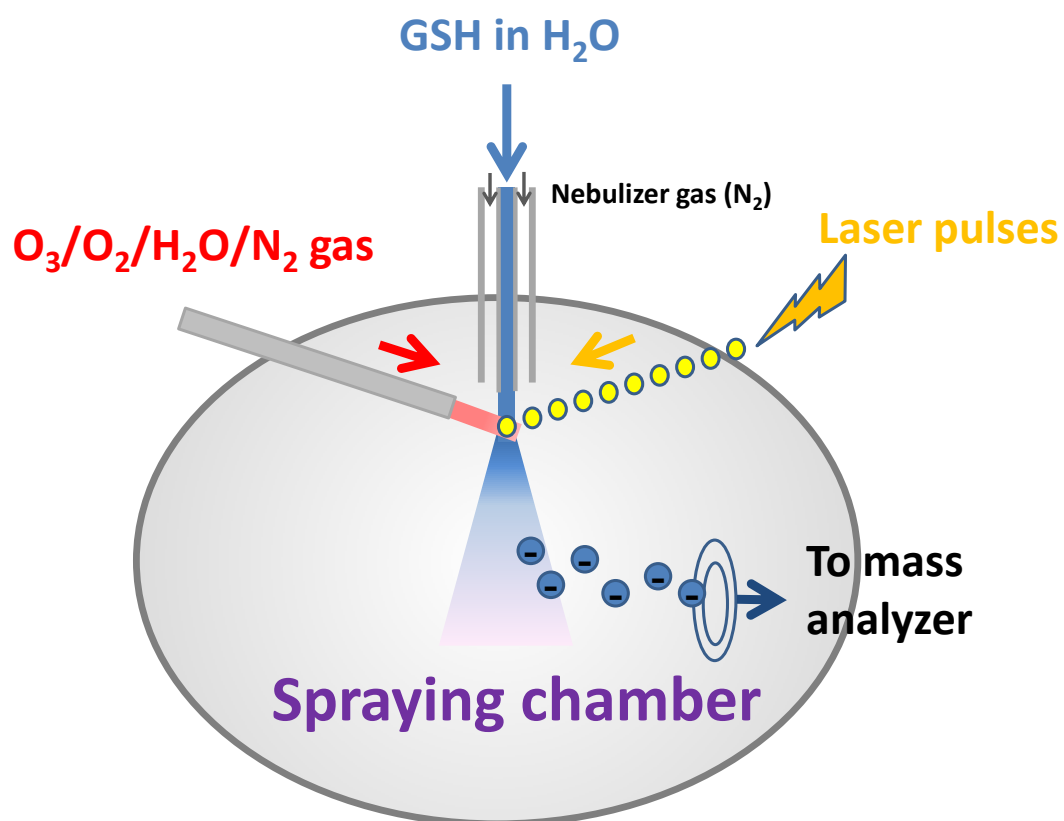


Figure S1 - Schematic diagram of setup used to study the OH radical + GSH reaction at the air-water interface.

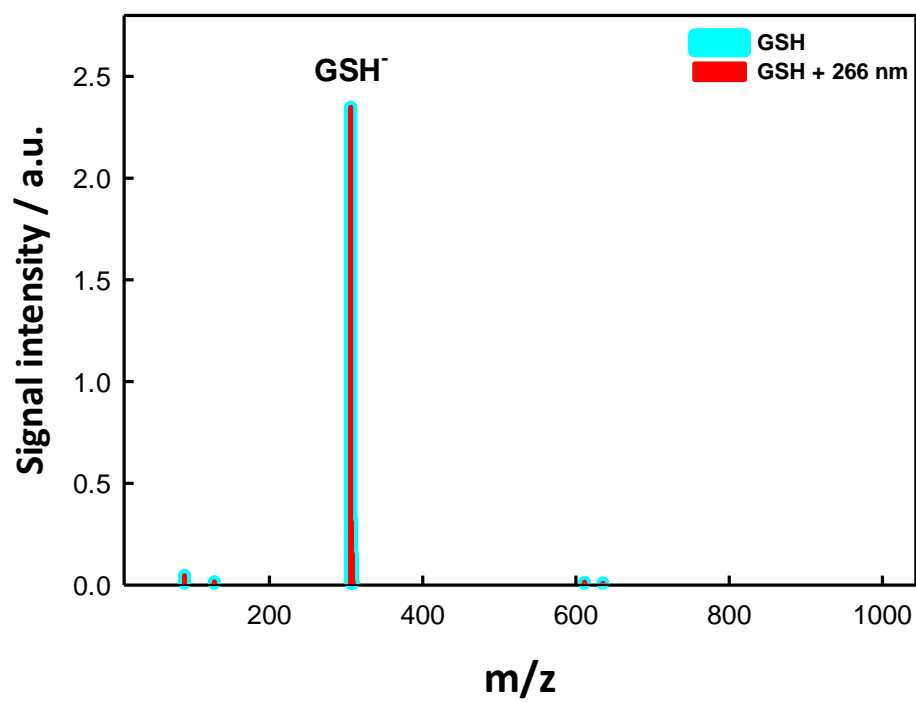


Figure S2 Negative ion electrospray mass spectrum of 0.1 mM GSH microjets (pH 4.4) in the absence (cyan)/presence (red) of 266 nm laser beam irradiation at 40 mJ pulse<sup>-1</sup> (maximum power) under H<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub> atmosphere.

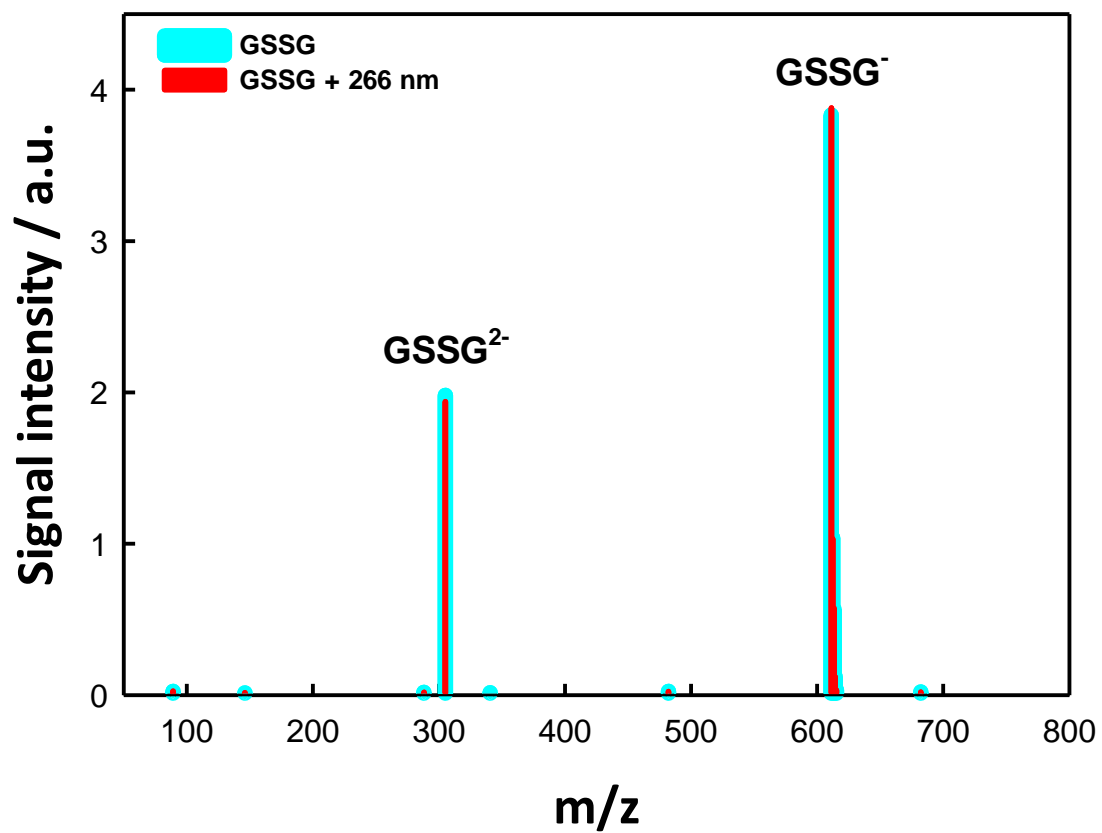


Figure S3 Negative ion electrospray mass spectrum of 1 mM GSSG microjets (pH 3.4) in the absence (cyan)/presence (red) of 266 nm laser beam irradiation at 40 mJ pulse<sup>-1</sup> (maximum power) under H<sub>2</sub>O/O<sub>2</sub>/N<sub>2</sub> atmosphere.

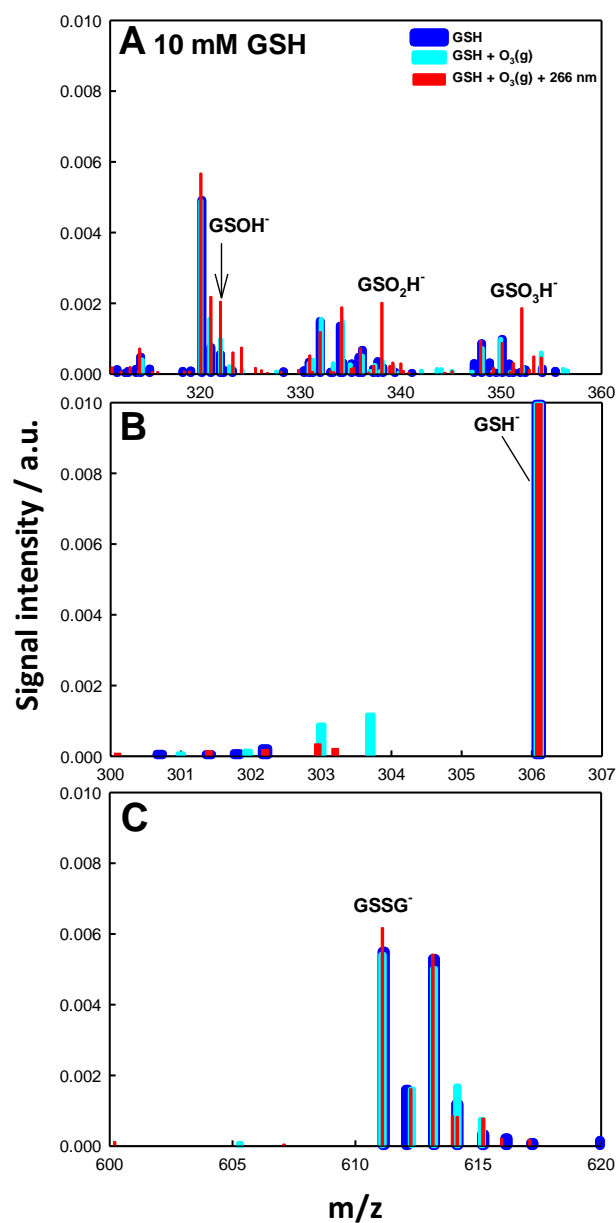


Figure S4 Negative ion ES mass spectra of aqueous 10 mM GSH (pH 3.1) microjets in O<sub>2</sub>(g)/H<sub>2</sub>O(g)/N<sub>2</sub>(g) mixtures (blue) or exposed to ~ 160 ppmv O<sub>3</sub>(g) in O<sub>2</sub>(g)/H<sub>2</sub>O(g)/N<sub>2</sub>(g) mixtures without (cyan)/with (red) 40 mJ 266 nm pulses. ([OH(g)]<sub>0</sub> ≤ 14 ppmv). 1 ppmv = 2.46 × 10<sup>13</sup> molecules cm<sup>-3</sup>. Note the absence of signals at m/z = 305 and 611 under 266 nm irradiation (red).



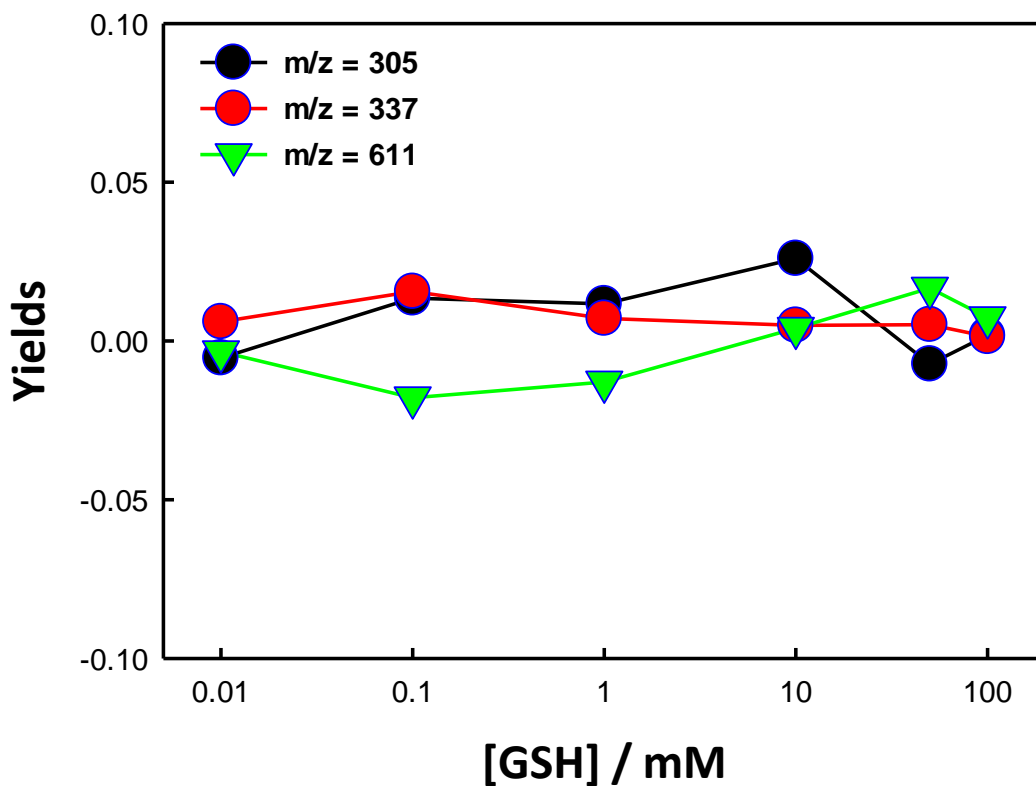


Figure S5 The  $m/z = 305$ ,  $337$ , and  $611$  products yields derived from signal intensities of the products divided by the decrease of the  $m/z = 306$  (GSH<sup>-</sup>) reactant under identical  $[\cdot\text{OH}(\text{g})] \leq 15$  ppmv ( $1 \text{ ppmv} = 2.46 \times 10^{13} \text{ molecules cm}^{-3}$ ) as a function of [GSH].

## SI REFERENCES

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