

**Supporting Information**

**for**

**Concentration Effects and Ion Properties Controlling the  
Fractionation of Halides during Aerosol Formation**

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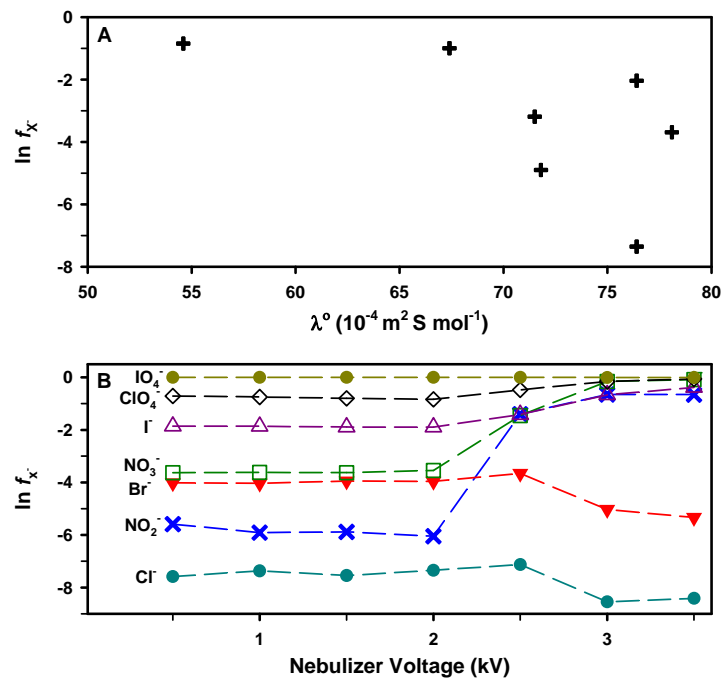
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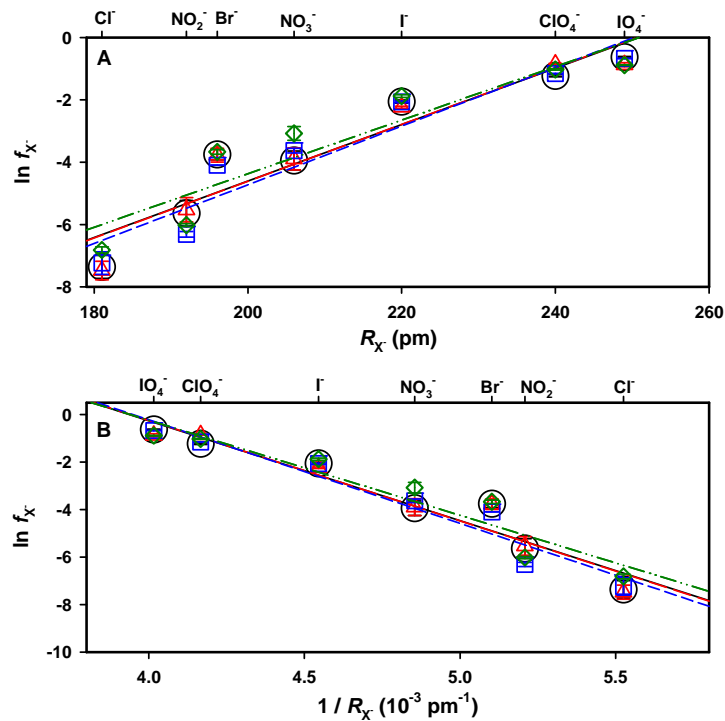
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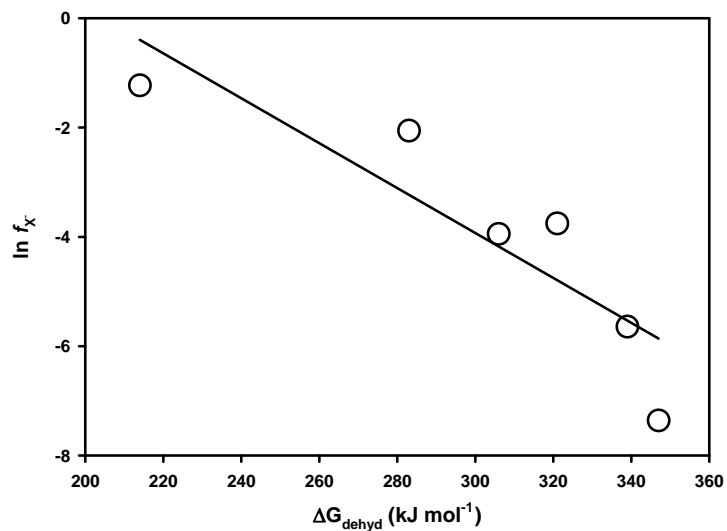
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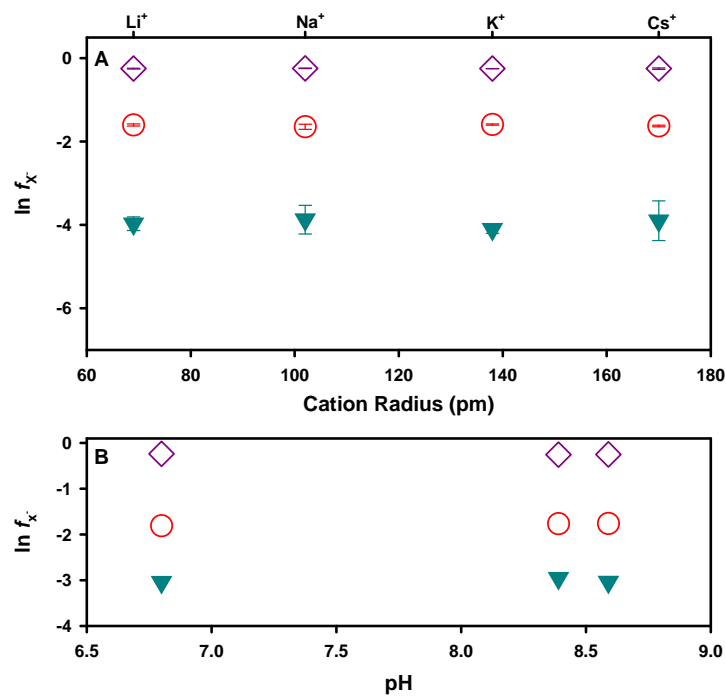
**Figure S1.** Anion fractionation,  $f_x^-$ , versus (A) the limiting equivalent ionic conductivity,<sup>1</sup>  $\lambda^o$ , and (B) nebulizer voltage for 100 nM equimolar solution of sodium salts of corresponding anions. The experimental conditions are the same as indicated in the experimental section of the main text.



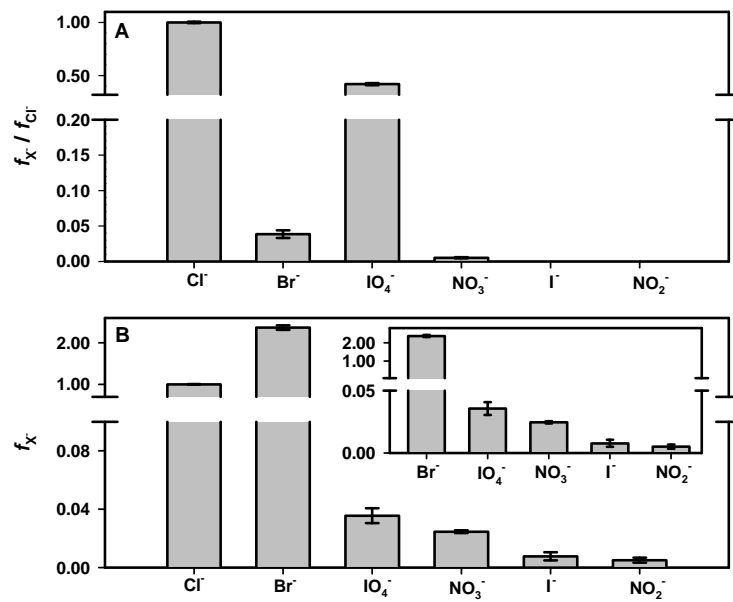
**Figure S2.** Anion fractionation,  $f_X^-$ , versus (A) anion radius,<sup>1</sup>  $R_X^-$ , and (B) reciprocal anion radius,  $R_X^{-1}$ . Dashed lines represent the linear fit with correlation coefficients ( $r^2$ ). The respective values of  $r^2$  for  $R_X^-$  and  $R_X^{-1}$ , are ( $\circ$ ) 0.901 and 0.935 for  $\text{H}_2\text{O}$ , ( $\Delta$ ) 0.898 and 0.934 for  $\text{D}_2\text{O}$ , ( $\diamond$ ) 0.908 and 0.907 for  $\text{CH}_3\text{OH}$ , and ( $\square$ ) 0.866 and 0.940 for  $\text{CH}_3\text{CH}_2\text{OH}$ . The experimental conditions are the same as indicated in the experimental section of the main text



**Figure S3.** Anion fractionation,  $f_X^-$ , versus anion dehydration free energy change,<sup>1</sup>  $\Delta G_{\text{dehyd}}$ , for a 100 nM equimolar solution. Solid line: linear fit with correlation coefficient  $r^2 = 0.786$ . The experimental conditions are the same as indicated in the experimental section of the main text.



**Figure S4.** Anion fractionation,  $f_x^-$ , versus (A) cationic radius<sup>1</sup> for 100 nM equimolar solution of halide salts of corresponding cations, and (B) pH for sodium salt solutions of (◇) I<sup>-</sup>, (○) Br<sup>-</sup>, and (▼) Cl<sup>-</sup>. Experimental conditions: Desolvation temperature 500 °C, cone voltage 80 V, needle voltage 1.5 kV, nitrogen nebulizing gas 70 psi.



**Figure S5.** Anion fractionation ratio to  $f_{Cl^-}$  at the air water interface for samples of monovalent anions with molar ratios found in seawater.<sup>2-6</sup> **(A)** Fractionation factors are normalized to  $f_{Cl^-} = 1$ . Sodium salts concentration for Sample **I** are 100  $\mu$ M Cl<sup>-</sup>, 0.44 nM NO<sub>2</sub><sup>-</sup>, 1.8 nM NO<sub>3</sub><sup>-</sup>, 121 nM Br<sup>-</sup>, 41 pM I<sup>-</sup>, 0.31 pM ClO<sub>4</sub><sup>-</sup>; and 100 nM IO<sub>4</sub><sup>-</sup>. **(B)** Sodium salts concentration for sample **II** with the molar ratios for a 10-times dilution of anions in seawater, with the exception of Cl<sup>-</sup> that is 1000 times diluted: 545  $\mu$ M Cl<sup>-</sup>, 239 nM NO<sub>2</sub><sup>-</sup>, 957 nM NO<sub>3</sub><sup>-</sup>, 66.24  $\mu$ M Br<sup>-</sup>, 22.2 nM I<sup>-</sup>, 0.17 nM ClO<sub>4</sub><sup>-</sup>, and 100 nM IO<sub>4</sub><sup>-</sup>. All other experimental conditions are the same as indicated in the experimental section of the main text.

## References

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