Supporting Information

Tobo et al. 10.1073/pnas.1008235107

SI Text

The equilibrium constants for reactions **1** and **2** can be expressed with a combination of the partial pressures of gaseous species, the water activity (a_w) and the activities of aqueous solutions (see Table S1). Here we assumed the CO_2 mixing ratio of 380 parts per million by volume (ppmv). In equilibrium with water vapor, a_w is equivalent to relative humidity (R.H.). The activities of aqueous solutions of $Ca(NO_3)_2$ and $CaCl_2$ are represented as $4\gamma_\pm{}^3 m^3$, where $\gamma_\pm$ is their mean activity coefficient and m is their molality. The temperature and molality dependences of $\gamma_\pm$ for these aqueous solutions were predicted using ion-interaction models (1–3). The water activity dependences of m for the aqueous solutions were taken from Kelly and Wexler (4). The equilibrium constant can also be expressed as a function of temperature, T, as follows (4):

$$K(T) = K(T_0)\exp\left\{-\frac{\Delta H^0}{RT_0}\left(\frac{T_0}{T}-1\right) - \frac{\Delta c_p^0}{R}\left[1+\ln\left(\frac{T_0}{T}\right)-\frac{T_0}{T}\right]\right\} \quad \textbf{[S1]}$$

where $K(T_0)$ is the equilibrium constant at a reference temperature ($T_0 = 298.15$ K) and is given by $\exp(-\Delta G^0/RT_0)$. ΔG^0 and ΔH^0 are the standard Gibbs energy change of the reaction and the standard enthalpy change of the reaction at T_0, respectively, in $\mathrm{J\,mol^{-1}}$. R and Δc_p^0 are the gas constant and the heat capacity change at T_0, respectively, in $\mathrm{J\,K^{-1}\,mol^{-1}}$. Thus, the concentrations of HNO_3 and HCl at equilibrium for reaction **1** ($[HNO_3]_e$ and $[HCl]_e$, respectively) and the ratios of HNO_3 to HCl at equilibrium for reaction **2** ($[HNO_3/HCl]_e$) were determined as functions of temperature and R.H.. The $[HNO_3]_e$, $[HCl]_e$, and $[HNO_3/HCl]_e$ values at regular intervals are contained in Tables S2, S3, and S4. The thermodynamic data used in the calculations are listed in Table S5.

1. Oakes CS, Felmy AR, Sterner SM (2000) Thermodynamic properties of aqueous calcium nitrate $\{Ca(NO_3)_2\}$ to the temperatures 373 K including new enthalpy of dilution data. *J Chem Thermodynamics* 32:29–54.
2. Ananthaswamy J, Atkinson G (1985) Thermodynamics of concentrated electrolyte mixtures. 5. A review of thermodynamic properties of aqueous calcium chloride in the temperature range 273.15–373.15 K. *J Chem Eng Data* 30:120–128.
3. Bradley DJ, Pitzer KS (1979) Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hückel parameters to 350 °C and 1 kbar. *J Phys Chem* 83:1599–1603.
4. Kelly JT, Wexler AS (2005) Thermodynamics of carbonates and hydrates related to heterogeneous reactions involving mineral aerosol. *J Geophys Res* 110:D11201 doi:10.1029/2004JD005583.

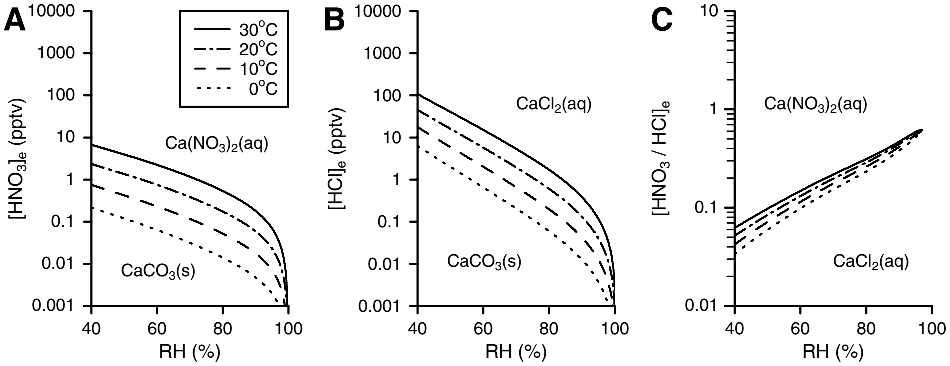

Fig. S1. Temperature and R.H. dependence of (*A*) $[HNO_3]_e$, (*B*) $[HCl]_e$ for reaction **1**, and (*C*) $[HNO_3/HCl]_e$ for reaction **2**.

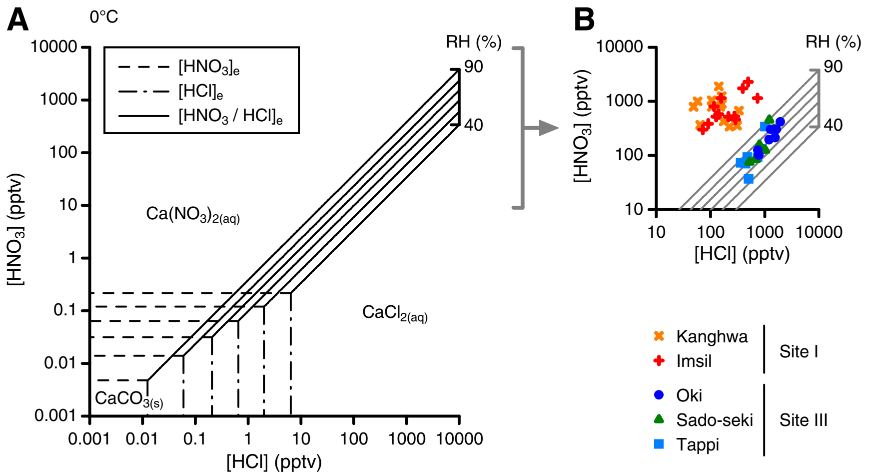

Fig. S2. Relationship of the concentration of HNO_3 and HCl with reactions **1** and **2**. (*A*) R.H. dependence of $[HNO_3]_e$, $[HCl]_e$, and $[HNO_3/HCl]_e$ at 0 °C. (*B*) Measured values of HNO_3 and HCl at Kanghwa, Imsil, Oki, Sado-seki, and Tappi from March to May 2007.

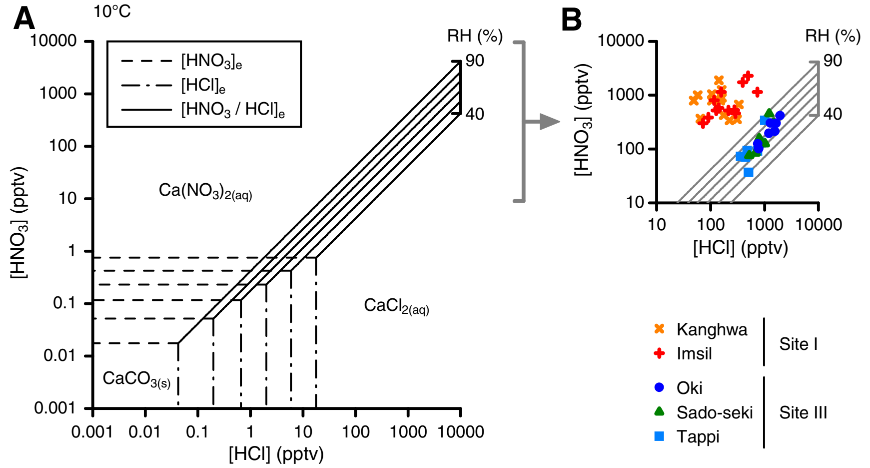

Fig. S3. Same as Fig. S2, but for R.H. dependence of $[HNO_3]_e$, $[HCl]_e$, and $[HNO_3/HCl]_e$ at 10 °C.

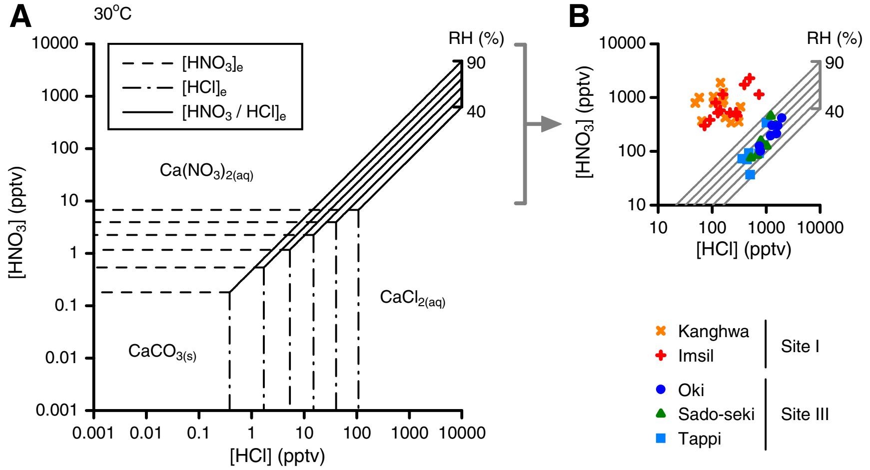

Fig. S4. Same as Fig. S2, but for R.H. dependence of $[HNO_3]_e$, $[HCl]_e$, and $[HNO_3/HCl]_e$ at 30 °C.

Table S1. Equilibrium relations and constants for reactions 1 and 2

Reaction*	Equilibrium constant expression[†]
$CaCO_{3(s)} + 2HX_{(g)} \leftrightarrow CaX_{2(aq)} + H_2O_{(aq)} + CO_{2(g)}$	$K = \frac{4(Y_{\pm}m)^3_{CaX_2} a_w p_{CO_2}}{p^2_{HX}}$
$Ca(NO_3)_{2(aq)} + 2HCl_{(g)} \leftrightarrow CaCl_{2(aq)} + 2HNO_{3(g)}$	$K = \frac{4(Y_{\pm}m)^3_{CaCl_2} p^2_{HNO_3}}{4(Y_{\pm}m)^3_{Ca(NO_3)_2} p^2_{HCl}}$

*X is NO_3 or Cl.

[†] p_{CO_2} is the partial pressure of CO_2 in bar, and p_{HX} is the partial pressure of HX in bar.

Table S2. Values of $[HNO_3]_e$ at regular intervals of temperature and R.H.

	$[HNO_3]_e$ (pptv) at T °C				
R.H. (%)	0 °C	10 °C	20 °C	25 °C	30 °C
40	0.2158	0.7504	2.3499	4.0183	6.7302
45	0.1606	0.5637	1.7823	3.0625	5.1545
50	0.1197	0.4240	1.3533	2.3365	3.9512
55	0.0883	0.3159	1.0180	1.7659	3.0004
60	0.0641	0.2315	0.7531	1.3127	2.2408
65	0.0455	0.1661	0.5455	0.9553	1.6383
70	0.0316	0.1164	0.3857	0.6783	1.1685
75	0.0214	0.0793	0.2648	0.4677	0.8088
80	0.0140	0.0520	0.1748	0.3095	0.5370
85	0.0086	0.0321	0.1080	0.1916	0.3329
90	0.0048	0.0175	0.0587	0.1039	0.1804
95	0.0019	0.0070	0.0228	0.0401	0.0692

Table S3. Values of $[HCl]_e$ at regular intervals of temperature and R.H.

	$[HCl]_e$ (pptv) at T °C				
R.H. (%)	0 °C	10 °C	20 °C	25 °C	30 °C
40	6.4127	17.7697	45.3885	70.6275	108.144
45	3.5300	10.1393	26.7781	42.3300	65.8037
50	2.0029	5.9136	16.0489	25.7089	40.4880
55	1.1457	3.4640	9.6288	15.6082	24.8695
60	0.6530	2.0176	5.7324	9.3937	15.1295
65	0.3690	1.1635	3.3735	5.5840	9.0838
70	0.2062	0.6625	1.9570	3.2696	5.3683
75	0.1132	0.3698	1.1112	1.8723	3.1005
80	0.0599	0.1987	0.6063	1.0295	1.7184
85	0.0295	0.0989	0.3058	0.5231	0.8795
90	0.0125	0.0423	0.1320	0.2272	0.3847
95	0.0038	0.0127	0.0399	0.0691	0.1178

Table S4. Values of $[HNO_3/HCl]_e$ at regular intervals of temperature and R.H.

	$[HNO_3/HCl]_e$ at T °C				
R.H. (%)	0 °C	10 °C	20 °C	25 °C	30 °C
40	0.0337	0.0422	0.0518	0.0569	0.0622
45	0.0455	0.0556	0.0666	0.0723	0.0783
50	0.0597	0.0717	0.0843	0.0909	0.0976
55	0.0771	0.0912	0.1057	0.1131	0.1206
60	0.0981	0.1147	0.1314	0.1397	0.1481
65	0.1234	0.1427	0.1617	0.1711	0.1804
70	0.1533	0.1756	0.1971	0.2075	0.2177
75	0.1890	0.2144	0.2383	0.2498	0.2609
80	0.2331	0.2618	0.2883	0.3007	0.3125
85	0.2922	0.3244	0.3531	0.3662	0.3785
90	0.3800	0.4149	0.4444	0.4573	0.4689
95	0.5190	0.5495	0.5719	0.5805	0.5875

Table S5. Summary of thermodynamic properties at 298.15 K (25 °C)[*]

Species	ΔG_f^0 (kJ mol^{-1})	ΔH_f^0 (kJ mol^{-1})	c_p^0 (J K^{-1} mol^{-1})
$CaCO_{3(s)}$	−1128.79	−1206.92	81.88
$Ca(NO_3)_{2(aq)}$	−776.09	−957.55	(−181)[†]
$CaCl_{2(aq)}$	−816.01	−877.13	(−275.7)[‡]
$HNO_{3(g)}$	−74.72	−135.06	53.35
$HCl_{(g)}$	−95.299	−92.307	29.12
$CO_{2(g)}$	−394.359	−393.509	37.11
$H_2O_{(aq)}$	−237.129	−285.83	75.291

[*] ΔG_f^0, ΔH_f^0, and c_p^0 are the Gibbs energy of formation, enthalpy of formation, and heat capacity at 298.15 K, respectively. All values are from ref. 1 unless otherwise indicated.

[†] Apparent heat capacity at infinite dilution from ref. 2.

[‡] Apparent heat capacity at infinite dilution from ref. 3.

1 Wagman DD, et al. (1982) The NBS tables of chemical thermodynamic properties—Selected values for inorganic and C_1 and C_2 organic substances in SI unites. *J Phys Chem Ref Data* 11:1–392.

2 Oakes CS, Felmy AR, Sterner SM (2000) Thermodynamic properties of aqueous calcium nitrate $\{Ca(NO_3)_2\}$ to the temperatures 373 K including new enthalpy of dilution data. *J Chem Thermodynamics* 32:29–54.

3 Ananthaswamy J, Atkinson G (1985) Thermodynamics of concentrated electrolyte mixtures. 5. A review of thermodynamic properties of aqueous calcium chloride in the temperature range 273.15–373.15 K. *J Chem Eng Data* 30:120–128.