Supporting Materials for

Metal complexation inhibits the effect of oxalic acid in aerosols as cloud condensation nuclei (CCN)

Takema FURUKAWA and Yoshio TAKAHASHI*

Department of Earth and Planetary Systems Science,

Graduate School of Science, Hiroshima University,

Higashi-Hiroshima, Hiroshima 739-8526, Japan

* Corresponding author

phone: +81-824-24-7460; fax: +81-824-24-0735;

e-mail: ytakaha@hiroshima-u.ac.jp

Table S1 List of sampling locations.

Observation station	Location name	Latitude (N)	Longitude (E)	Height (above S.L./m)
Beijing	Institute of Atmospheric Physics	39.93	116.35	100
Tsukuba	Geological Survey of Japan	36.06	140.14	44
Hedo	Cape of Hedo	26.87	128.26	60

Table S2. Concentrations (dC/dlogD (nmol/m^3)) of non-sea salt sulfate (nss-sulfate) and total sulfate, and the ratio of [nss-sulfate]/[total sulfate] (%) in aerosols in (a) winter and (b) summer.

(a)

Winter					
Diameter range (μm)	Mean size (μm)	dlogD	nss- SO_4^{2-} (nmol/m^3) *3	total SO_4^{2-} (nmol/m^3) *3	nss-sulfate / total SO_4^{2-} (%)
0.08-0.43 *1	0.25	0.73	6.28	6.28	100
0.65-0.43	0.54	0.18	8.57	8.57	100
1.1-0.65	0.88	0.23	9.73	9.73	100
2.1-1.1	1.6	0.28	3.67	3.72	98.2
3.3-2.1	2.7	0.20	1.69	1.91	88.6
4.7-3.3	4.0	0.15	0.831	1.29	64.5
7.0-4.7	5.9	0.17	0.641	1.02	62.7
11-7.0	9.0	0.20	0.270	0.492	54.9
11-20 *2	15.5	0.44	0.532	0.893	59.8
-	-	Total	32.2	33.9	95.0

(b)

Summer					
Diameter range (μm)	Mean size (μm)	dlogD	nss- SO_4^{2-} (nmol/m^3) *3	total SO_4^{2-} (nmol/m^3) *3	nss-sulfate / total SO_4^{2-} (%)
0.08-0.43 *1	0.25	0.73	9.56	9.56	100
0.65-0.43	0.54	0.18	18.7	18.5	100
1.1-0.65	0.88	0.23	25.5	25.5	100
2.1-1.1	1.6	0.28	17.9	18.0	99.6
3.3-2.1	2.7	0.20	6.26	7.06	88.7
4.7-3.3	4.0	0.15	1.95	3.39	57.4
7.0-4.7	5.9	0.17	1.23	2.35	52.4
11-7.0	9.0	0.20	0.724	1.17	62.0
11-20 *2	15.5	0.44	2.27	2.67	85.2
-	-	Total	84.1	88.2	95.3

*1 Minimum size of the stage was assumed as 0.08 μm.
*2 Maximum size of the stage was assumed as 20 μm.
*3 Concentration as measured (before normalized by dlogD).

Table S3. Concentrations (nmol/m^3; before normalized by dlogD) of water soluble components in aerosols; (a) winter, (b) summer, and (c) winter/summer.

(a) Winter (January 21 to February 12, 2002)

Diameter range (μm)	Mean size (μm)	dlogD	Oxalate	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	NH_4^+	Mg^{2+}	Zn^{2+}
0.08-0.43	0.25	0.73	0.471	1.27	3.56	6.28	0.0686	-	49.2	-	0.0774
0.65-0.43	0.54	0.18	0.394	1.59	3.91	8.57	0.0616	-	44.5	-	0.140
1.1-0.65	0.88	0.23	0.444	5.77	10.1	9.73	0.222	-	85.8	0.0255	0.343
2.1-1.1	1.6	0.28	0.305	1.70	3.19	3.72	0.400	1.34	15.1	0.104	0.395
3.3-2.1	2.7	0.20	0.168	1.71	2.60	1.91	1.34	4.24	2.64	0.228	0.324
4.7-3.3	4.0	0.15	0.0903	2.79	2.48	1.29	1.38	8.91	-	0.228	0.143
7.0-4.7	5.9	0.17	0.0821	2.06	1.92	1.02	1.51	7.45	-	0.223	0.0714
11-7.0	9.0	0.20	0.0368	1.00	0.740	0.492	0.824	4.34	-	0.0774	0.0234
11-20	15.5	0.44	0.0770	1.75	1.28	0.893	1.92	7.00	-	0.151	0.0246

(b) Summer (July 28 to August 13, 2002)

Diameter range (μm)	Mean size (μm)	dlogD	Oxalate	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	NH_4^+	Mg^{2+}	Zn^{2+}
0.08-0.43	0.25	0.73	0.0730	0.123	0.193	9.56	0.0307	-	51.2	-	0.0584
0.65-0.43	0.54	0.18	0.230	0.220	0.252	18.7	0.0536	-	93.6	-	0.0866
1.1-0.65	0.88	0.23	0.338	0.105	0.524	25.5	0.186	-	78.9	-	0.232
2.1-1.1	1.6	0.28	0.426	0.196	0.834	17.9	0.389	1.25	37.5	1.31	0.448
3.3-2.1	2.7	0.20	0.520	1.42	4.50	7.06	0.942	15.6	5.22	1.49	0.390
4.7-3.3	4.0	0.15	0.314	3.42	8.09	3.39	1.61	28.2	-	0.849	0.191
7.0-4.7	5.9	0.17	0.161	3.52	7.34	2.35	2.14	21.8	-	0.915	0.113
11-7.0	9.0	0.20	0.0844	1.42	4.12	1.17	1.57	8.64	-	0.668	0.0548
11-20	15.5	0.44	0.0955	1.53	1.65	2.67	3.94	7.70	-	0.328	0.0744

(c) Winter / Summer

Diameter range (μm)	Mean size (μm)	dlogD	Oxalate	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	NH_4^+	Mg^{2+}	Zn^{2+}
0.08-0.43	0.25	0.73	4.76	7.52	13.4	0.477	1.65	-	0.701	-	0.971
0.65-0.43	0.54	0.18	0.308	1.30	2.79	0.0826	0.205	-	0.086	-	0.292
1.1-0.65	0.88	0.23	0.304	12.7	4.44	0.0876	0.258	-	0.251	-	0.338
2.1-1.1	1.6	0.28	0.202	2.44	1.07	0.0582	0.288	0.300	0.113	0.0224	0.247
3.3-2.1	2.7	0.20	0.0646	0.240	0.116	0.0542	0.284	0.0546	0.101	0.0306	0.165
4.7-3.3	4.0	0.15	0.0432	0.122	0.0461	0.0570	0.129	0.0476	-	0.0404	0.113
7.0-4.7	5.9	0.17	0.0869	0.100	0.0445	0.0745	0.120	0.0583	-	0.0413	0.107
11-7.0	9.0	0.20	0.0872	0.141	0.0360	0.0842	0.104	0.100	-	0.0232	0.0850
11-20	15.5	0.44	0.354	0.502	0.340	0.147	0.214	0.400	-	0.203	0.147

Table S4. Correlation coefficient (R^2) between some ions at various particle diameters.

Winter

	Oxalate	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	NH_4^+	Mg^{2+}
Oxalate	1.00							
Cl^-	0.458	1.00						
NO_3^-	0.700	0.920	1.00					
SO_4^{2-}	0.884	0.565	0.796	1.00				
Ca^{2+}	0.282	8.12×10^{-3}	0.0971	0.321	1.00			
Na^+	0.434	0.0370	0.196	0.434	0.850	1.00		
NH_4^+	0.695	0.642	0.831	0.921	0.340	0.425	1.00	
Mg^{2+}	0.113	1.27×10^{-3}	0.0490	0.211	0.884	0.685	0.296	1.00
Zn^{2+}	0.561	0.379	0.445	0.320	1.60×10^{-5}	0.0548	0.168	0.0621

Summer

	Oxalate	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Na^+	NH_4^+	Mg^{2+}
Oxalate	1.00							
Cl^-	0.0140	1.00						
NO_3^-	4.03×10^{-4}	0.943	1.00					
SO_4^{2-}	0.432	0.333	0.287	1.00				
Ca^{2+}	0.0240	0.791	0.812	0.352	1.00			
Na^+	2.82×10^{-3}	0.913	0.951	0.303	0.650	1.00		
NH_4^+	0.132	0.406	0.418	0.815	0.498	0.427	1.00	
Mg^{2+}	0.183	0.654	0.774	0.0790	0.507	0.814	0.292	1.00
Zn^{2+}	0.899	0.025	6.72×10^{-4}	0.357	0.0160	1.40×10^{-4}	0.0608	0.170

Table S5. The R factors of Ca K-edge XANES fitting and Zn K-edge XANES and EXAFS fitting.

Winter

Particle diameter (μm)	Ca-XANES	Zn-XANES	Zn-EXAFS
> 11	0.00117	0.000998	-
11–7.0	0.000773	0.00228	-
7.0–4.7	0.000698	0.000422	-
4.7–3.3	0.000749	0.000245	-
3.3–2.1	0.000170	0.00210	0.0349
2.1–1.1	0.000904	0.000248	0.0340
1.1–0.65	0.00104	0.00263	0.0289
0.65–0.43	0.00132	0.000732	0.0212
< 0.43	-	0.00169	-

Summer

Particle diameter (μm)	Ca	Zn	Zn-EXAFS
> 11	0.00124	0.000921	-
11–7.0	0.00107	0.000481	-
7.0–4.7	0.000846	0.00198	-
4.7–3.3	0.000680	0.000331	-
3.3–2.1	0.00255	0.000154	0.0296
2.1–1.1	0.000512	0.000527	0.0370
1.1–0.65	0.000891	0.00553	-
0.65–0.43	-	0.000560	0.0301
< 0.43	-	0.00172	-

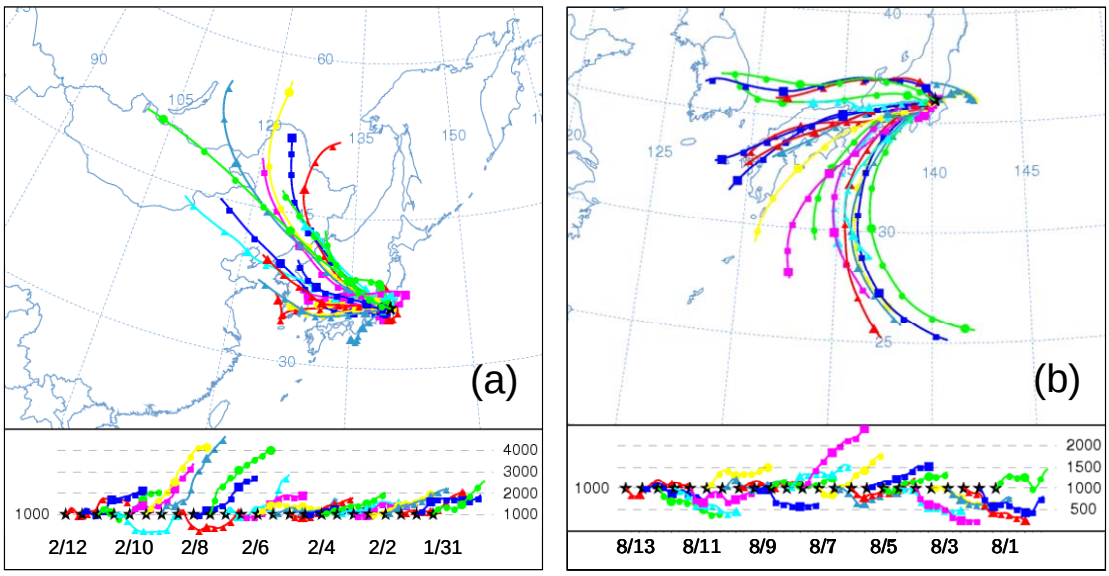

Figure S1. Three dimensional backward trajectory analysis in sampling periods; (a) winter; (b) summer. The NOAA/ARL HYSPLIT model (Draxler and Rolph, 2003) was used for the calculation. The trajectories started at the altitude of 1000 m above the sampling site in Tsukuba.

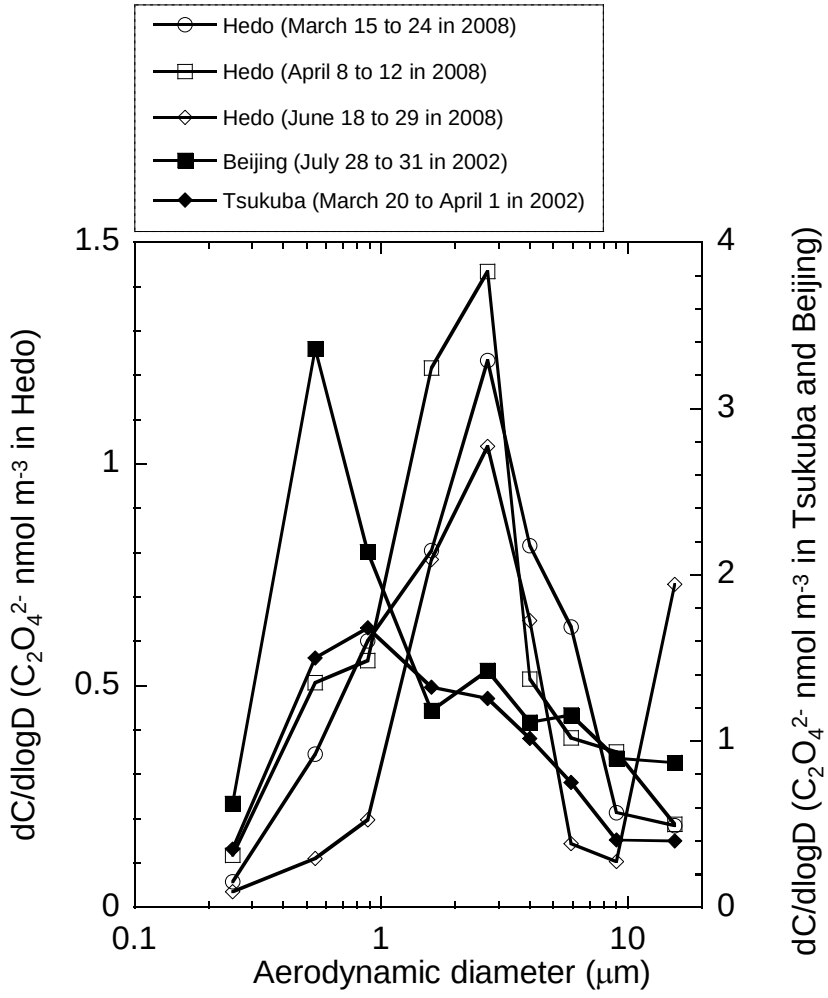

Figure S2. Size distribution of oxalic acid in aerosols at various sites.

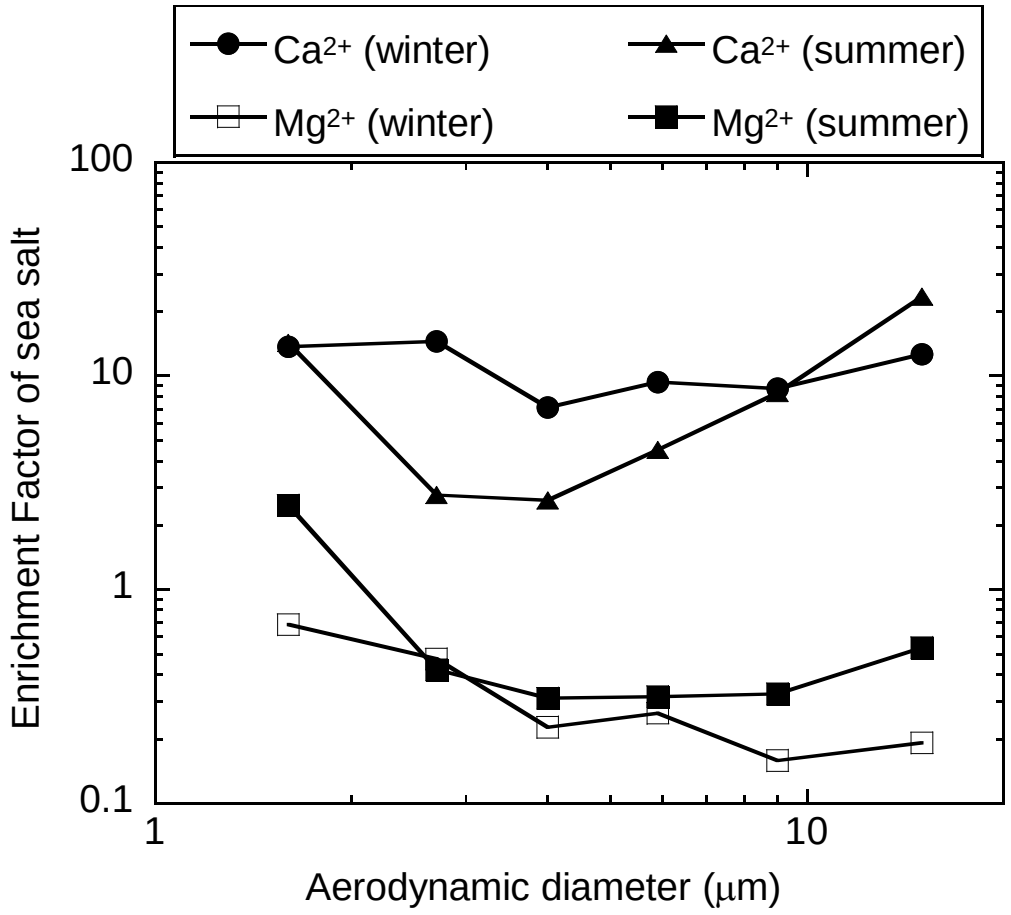

Figure S3. Enrichment Factor of sea salt particles of Ca^{2+} and Mg^{2+} in each period.

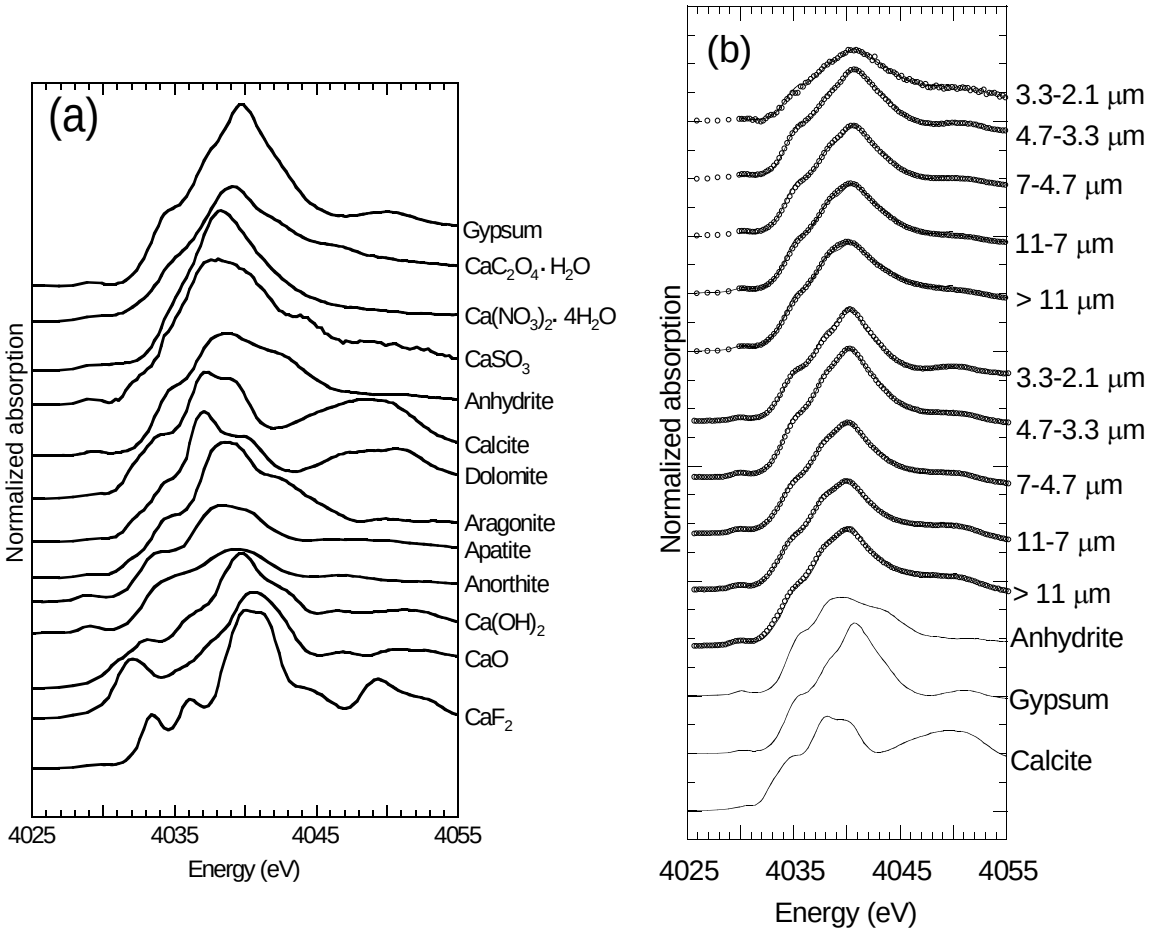

Figure S4. Calcium K-edge XANES; (a) Ca standard materials; (b) coarse particle samples (open circle: samples; lines: fitting) during winter and summer at Tsukuba with standard materials used for fitting.

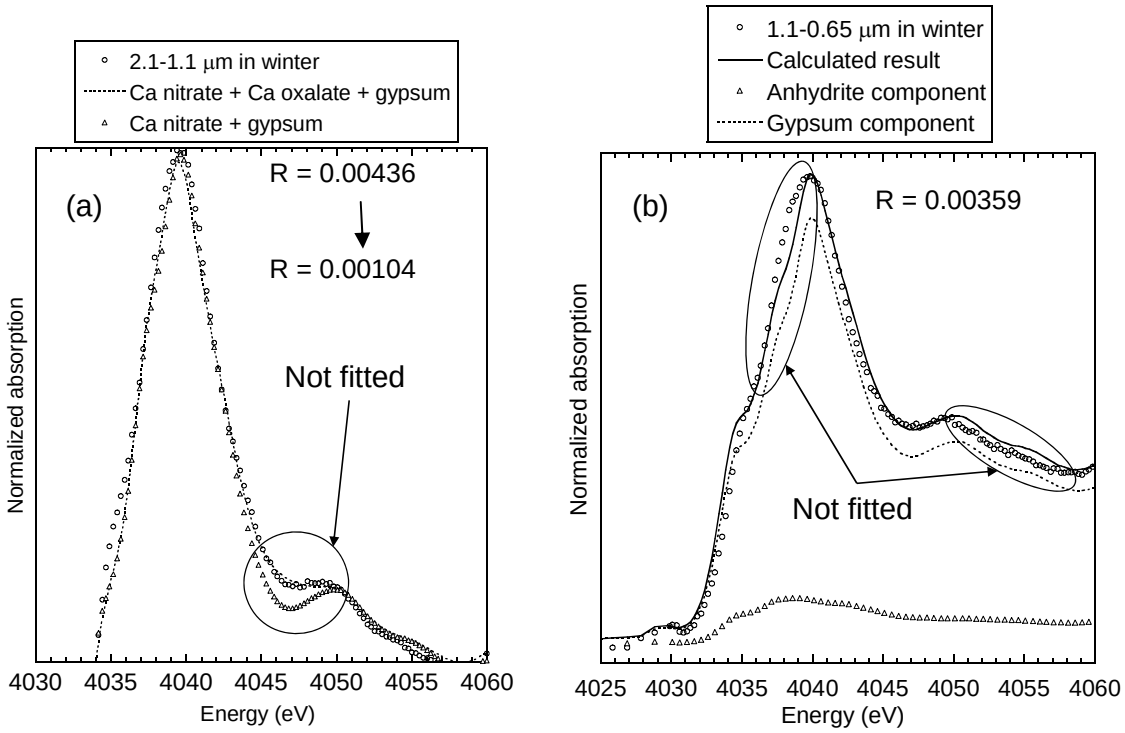

Figure S5. Fitting results of the samples with various standard materials. A circle and ellipses represent the regions of misfit. (a) fitting by Ca nitrate + Ca oxalate + gypsum (dashed line, R = 0.00104), Ca nitrate + gypsum (triangle, R = 0.00436), and aerosol samples of 2.1-1.1 μm in winter (circle). (b) fitting result (line) by gypsum (triangle) + anhydrite (triangle) with the spectrum of 1.1-0.65 μm in winter (circle), and R = 0.00359.

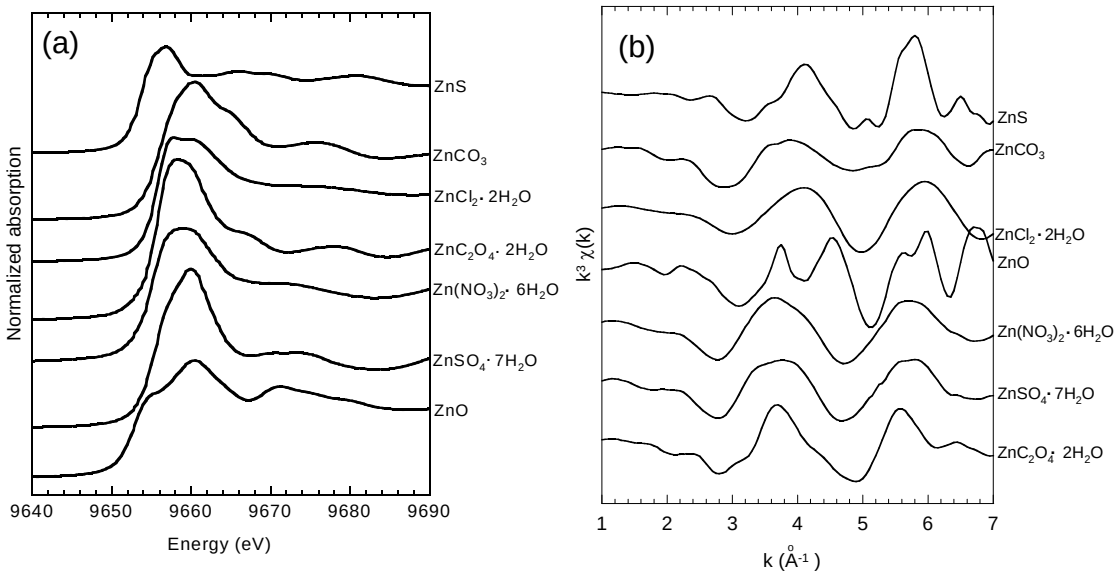

Figure S6. Zinc K-edge XANES (a) and EXAFS (b) for Zn standard materials.

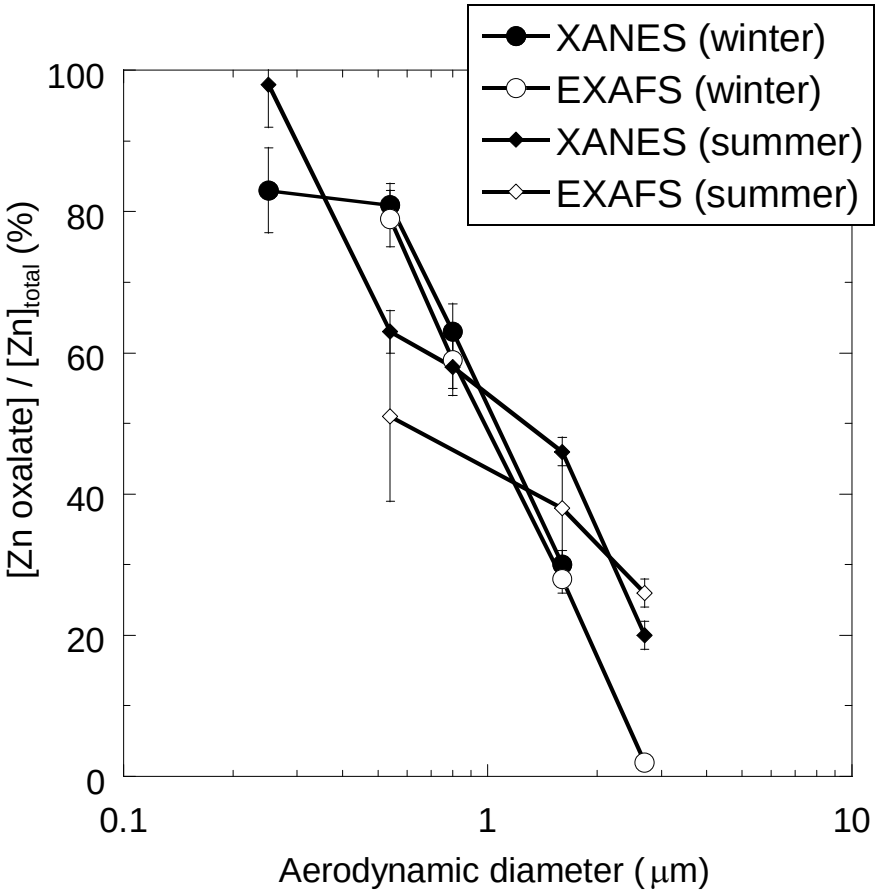

Figure S7. Comparison of the fraction of Zn oxalate resulting from XANES fitting and EXAFS fitting, which shows the consistency between them.