Characterization of seasonal sea-salt particles in Antarctica by the combined use of low-Z particle electron probe X-ray microanalysis and Raman microspectrometry

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Introduction

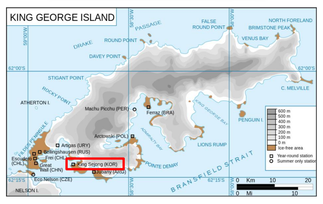
Antarctica, having minimal influence from trade-winds, is isolated from cross-continental anthropogenic aerosol sources. Hence, it is one of the few pristine sites ideal for studying natural sea salt aerosols (SSAs) processes (Maskey et al., 2011). The different phases of natural SSAs significantly affect earth's radiative balance by scattering light and acting as cloud droplet or ice-nuclei (Ault et al., 2013). So far most investigations are based on artificially generated SSAs. This study aims to present a systematic examination of the inter-dependence of hygroscopic properties and the chemical heterogeneity of natural SSAs collected in the Antarctic.

Aerosol samples were collected at a Korean scientific research station in the Antarctic: the King Sejong station (62°22'S, 58°78'W). Sea salt particles were collected on Al foils (Aldrich, 99.8% purity) using a three stage cascade impactor (PM_{10} Impactor, Dekati Inc.) in different seasons. The impactor has aerodynamic cut-offs of 10, 2.5, and 1 μm for stages 1, 2, and 3, respectively, at a 10 L min^{-1} sampling flow. The chemical compositions, mixing states, and spatial distribution of chemical species within individual particles are obtained by the combined use of low-Z particle energy-dispersive X-ray microanalysis and Raman microspectrometry.

Material and Methods

1. Sampling :

- *Sampling methods*
  - **3-stage Dekati PM_{10} impactor**
  - **Aerodynamic cut-offs : 10, 2.5, 1 μm**
  - **Substrate : Al foil (Sigma-Aldrich, 99.8% purity)**
  - **Sampling flow : 10 L min^{-1}**



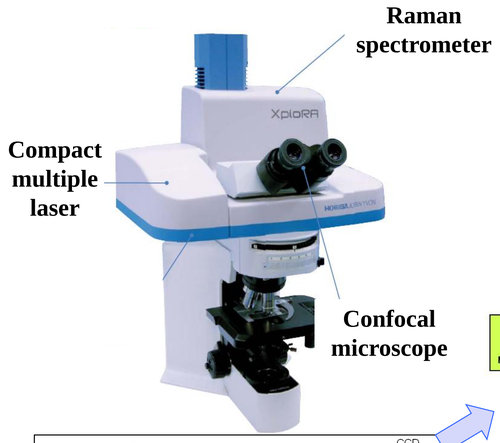
- *Sampling site*
  - **The King Sejong station (62°22'S, 58°78'W)**

- *Samples*

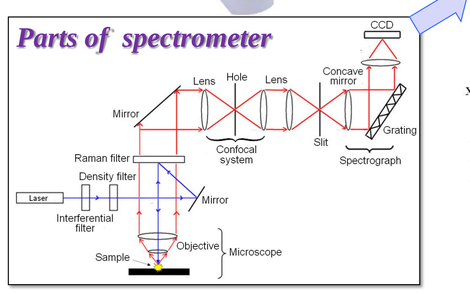
Season	Year	Month	Date	Stage	Sea Temp. (℃)	Chl-a (μg/L)	Temp. (℃)
Summer	2011	12	9	2	0.6	123.0	1.1
Winter	2012	7	23	2	-1.6	6.3	0.4

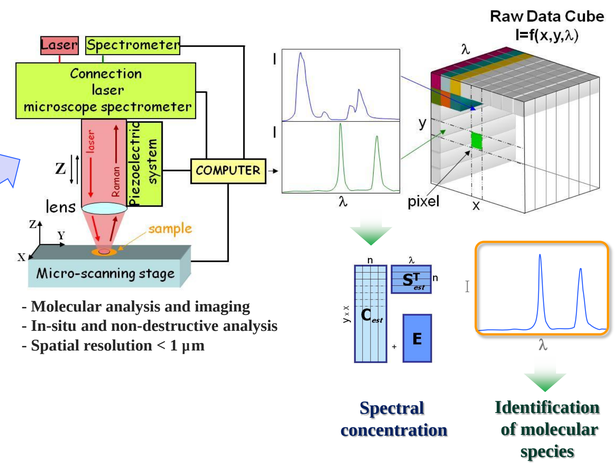
2. Measurement and Analysis :

- *Micro-Raman spectrometry for single particle analysis*



- **XploRA, Horiba (Jobin Yvon, Horiba)**
- **532 nm laser and 1800 gr/m**
- **100X objective with a 0.9 NA**
- **Spectra in the range of 500 to 4000 cm^{-1}**
- **Acquisition time : 5~10s**





- Molecular analysis and imaging
- In-situ and non-destructive analysis
- Spatial resolution < 1 μm

- *Particle morphology and X-ray mapping measurement using SEM/EDX*

❖ **SEM-EDX (Scanning Electron Microscopy–Energy Dispersive X-ray Spectrometry)**
- **Individual Particle Analysis:**
  - **shape and size: secondary / backscattered electron images**
  - **chemical composition: X-ray spectrum**

❖ **Ultra-thin window EDX for low-*Z* elements detection (C, N, O, F)**

❖ **Metallic collecting substrates for minimizing charging effects (Ag or Al)**

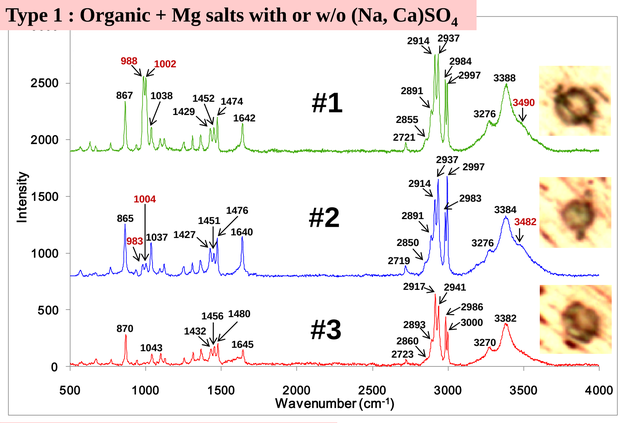
- **Jeol JSM-6390 SEM**
- **Oxford Link SATW ultrathin window EDX detector**
- **The detector resolution : 133 eV for Mn Kα X-rays**
- **10 kV accelerating voltage**
- **0.5 nA beam current**
- **Oxford INCA Energy software : X-ray spectra and elemental maps**

Results

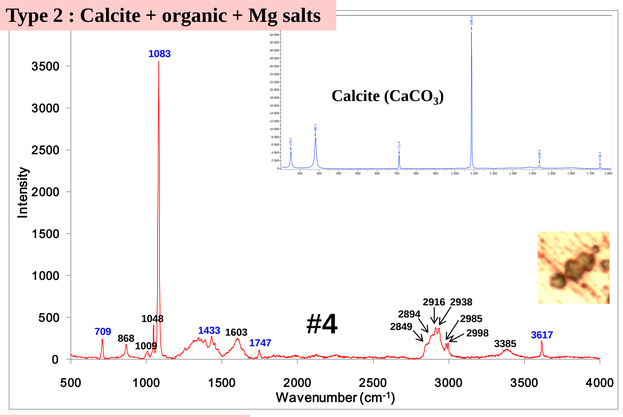
Typical Raman spectra of SSAs in Antarctica

Summer

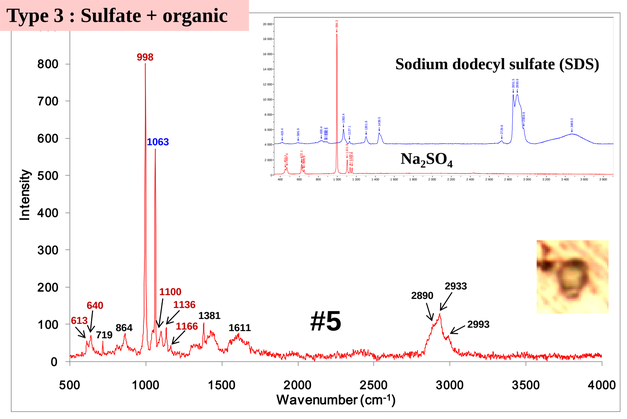
Type 1 : Organic + Mg salts with or w/o (Na, Ca)SO_4



Type 2 : Calcite + organic + Mg salts

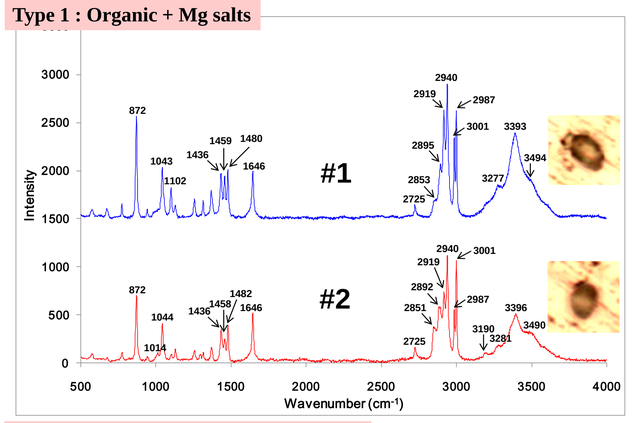


Type 3 : Sulfate + organic

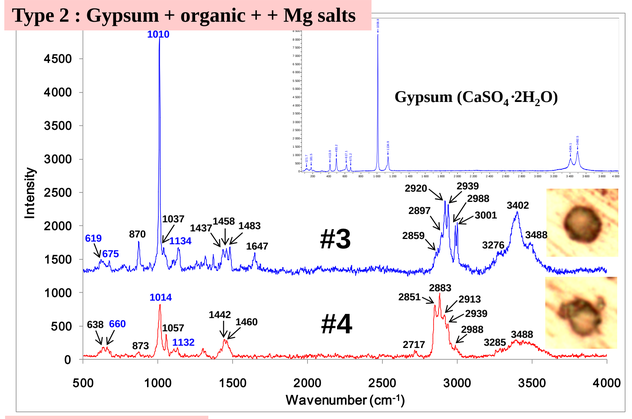


Winter

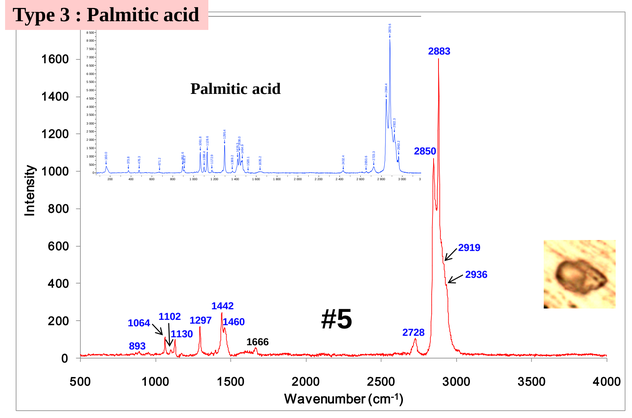
Type 1 : Organic + Mg salts



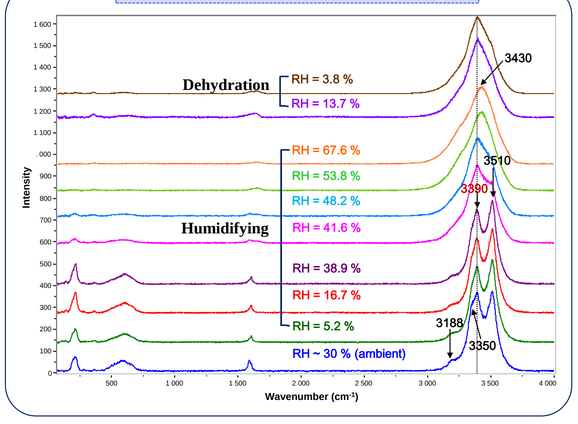
Type 2 : Gypsum + organic + + Mg salts



Type 3 : Palmitic acid



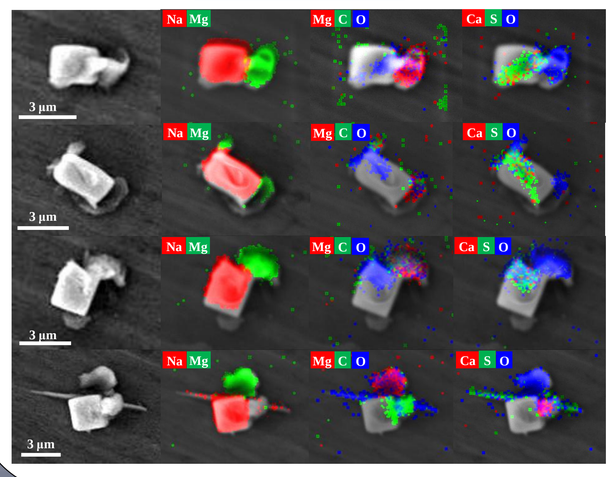
Results of standard $MgCl_2 \cdot 6H_2O$



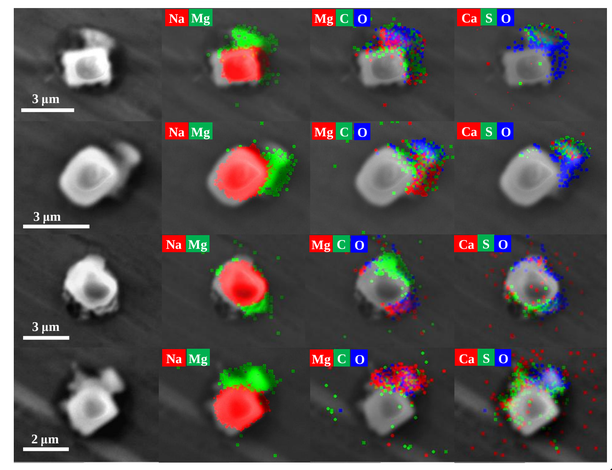
Frequencies										Vibration (Assignment)	Compounds
Summer					Winter						
1	2	3	4	5	1	2	3	4	5		
567 634 670 769	569 630 668 770	578 673 774	709	641 719	576 674 775	577 677 776	619 675 772	638 660		O=C-O angle deformation SO_4 out of phase bend sulfate(SO_4^{2-}) or O=C-O angle deformation O=C-O angle deformation CO_3 in-plane bend skeletal stretch	carboxylic acids (Na, Ca) SO_4 (Na, Ca) SO_4 carboxylic acids calcite ($CaCO_3$) Isopropyl group
867 938 988 1002 1038	865 936 983 1004 1037	870 942 1043	868 1009 1048	864 998 1047	872 945 1009 1044	872 946 1014 1044	870 945 1010 1038	873 1014 1057	870 893 1064	OO stretch C-C skeletal stretch symmetric COC stretch SO_4 i. ph. stretch symmetric sulfate(SO_4^{2-}) anti-symmetric C-C	Hydrogen peroxide n-alkanes aliphatic ethers n-alkanes gypsum or anhydrite n-alkanes
1097 1124	1096 1124	1103 1130	1083	1063 1100 1136	1102 1129	1102 1130	1135	1104 1132	1102 1130	trans chain C-C-C o. ph. stretch CO_3 i. ph. stretch CH_2 twist trans chain C-C-C i. ph. stretch	calcite ($CaCO_3$) n-alkanes n-alkanes
1254 1310 1365 1429 1452 1474	1254 1309 1365 1427 1451 1476	1258 1316 1368 1432 1456 1480	1433	1382 1427 1448	1257 1315 1370 1436 1459 1480	1259 1297 1318 1371 1436 1458 1482	1260 1315 1371 1437 1458 1483	1299 1316 1442 1460	1297 1399 1442 1460	oscillations involving C-O-H group CH_2 i. ph. twist CH_3 twist methylene deformation CH_3 symmetric deformation CH_2 + CH_3 o. ph. bend	n-alkanes n-alkanes n-alkanes
1642	1640	1645	1603 1747	1611	1646	1646	1647		1661	carbon(D) symmetric C=O stretch CO_3	graphitic carbon carboxylic acids calcite ($CaCO_3$)
2721 2855 2891 2914 2937 2984 2997	2719 2850 2891 2914 2937 2983 2997	2723 2860 2893 2917 2941 2986 3000	2849 2894 2916 2938 2985 2998	2890 2933 2993	2725 2853 2895 2919 2940 2987 3001	2725 2851 2892 2919 2940 2987 3001	2859 2897 2920 2939 2988 3001	2717 2851 2883 2913 2939 2988	2728 2850 2883 2919 2936	overtone of the 1376 cm^{-1} symmetric CH_2 stretch anti-symmetric CH_2 stretch symmetric CH_3 stretch anti-symmetric CH_3 stretch C=H stretch C=H stretch	n-alkanes n-alkanes n-alkanes n-alkanes n-alkenes n-alkenes
3276 3388 3490	3276 3384 3482	3270 3382	3385 3617		3277 3393 3494	3190 3281 3396 3490	3402 3488	3285 3394		OH stretch (crystalline water)	Mg salt Mg salt gypsum calcite ($CaCO_3$)

Typical element X-ray maps of SSAs in Antarctica

Summer



Winter



Discussion

Most of the sea salt particles have NaCl showing cubic structures in core and Mg^{2+} and organic species in boundaries. Raman signatures indicate presence of many organic species apparently from phytoplankton activity. The association of sulfate species with NaCl are more abundant in the summer than in the winter SSAs.

References

Ault, A. P., Moffet, R. C., Baltrusaitis, J., Collins, D. B., Ruppel, M. J., Cuadra-Rodriguez, L. A., Zhao, D., Guasco, T. L., Ebben, C. J., Geiger, F. M., Bertram, T. H., Prather, K. A., and Grassian, V. H. (2013). Environ. Sci. Technol., 47, 5603−5612.
Maskey, S., Geng, H., Song, Y.-C., Hwang, H., Yoon, Y.-J., Ahn, K.-H., and Ro, C.-U. (2011). Environ. Sci. Technol., 45, 6275–6282.
You,Y., R.-Wolff, L., and Bertram, A. K. (2013). Atmos. Chem. Phys., 13, 11723–11734