

Structural characterization of humic-like substances in atmospheric aerosols in Osaka, Japan

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Macromolecular organic substances in atmospheric aerosols have been termed humic-like substances (HULIS) and it can influence functions of aerosols, such as cloud nucleation, absorption of solar radiation, and transportation of pollutant. However, despite its importance in environment, a comprehensive understanding of the structure of the HULIS remains elusive. We therefore studied the structural features of the HULIS in urban aerosols and compared it with those of soil and aquatic humic substances (HS).

Samples and Experiment

Water soluble HULIS (WS-HULIS) was obtained from aerosol sample, which was collected in Osaka city, Japan in summer and autumn 2010, and was analyzed using high-performance size-exclusion chromatography (HPSEC), pyrolysis gas chromatography (py-GC), and liquid-state ¹³C NMR spectroscopy.

Results and Discussion

A weight-averaged molecular weight of the WS-HULIS was estimated 800–950 by HPSEC and molecular size distribution of the WS-HULIS was similar to that of the aquatic HS, particularly to fulvic acids. ¹³C NMR spectroscopy showed lower aromatic (16–19% of total C) and higher aliphatic carbon content (35–45%) of the WS-HULIS (Fig.1) as compared to those of the soil HS. This result also suggests the structural similarities between the WS-HULIS and the aquatic HS. However, contrary to previous study [1], signals of lignin derived structure (55, 150ppm), which are generally detected in the soil and aquatic HS, were not observed in the NMR spectra of the WS-HULIS in both summer and autumn. This observation is supported by py-GC using tetramethylammonium hydroxide.

In conclusion, average chemical structure of the WS-HULIS in aerosols is relatively similar to that of the aquatic HS rather than soil HS. However, the WS-HULIS used in this study has no lignin derived component, indicating that the origin of the WS-HULIS may differ from that of the soil and aquatic HS. The structural features of alkaline extractable HULIS will also be presented.

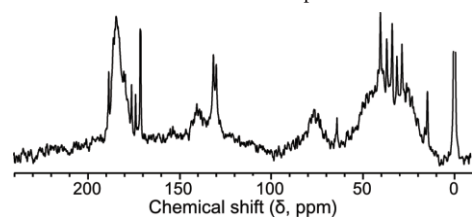


Figure 1: Liquid-state ¹³C NMR spectrum of the water soluble humic-like substances in aerosols collected in summer 2010

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[1] Duarte et al. (2007) *Atmos. Environ.* **41**, 8100-8113.

The role of contamination in the genesis of shoshonitic volcanism, central Pontide, Turkey

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Late Cretaceous (~ 80 Ma) subduction-related volcanic rocks are widespread in the central Pontides of Turkey, both in the Sinop area to the North and in the Alaçam-Dikmen-Durağan areas to the South. There are two distinct groups of lava in both areas in terms of K₂O. The northern area rocks display high-K calcalkaline or shoshonitic affinities, whereas the southern area rocks have either medium-K calcalkaline or shoshonitic affinities. The shoshonites are younger than calcalkaline rocks in both areas, but the northern shoshonites are more potassium-rich than the southern shoshonites. The chondrite-normalized trace element patterns of all the lavas are characterised by strong enrichments in LILE (Rb, Ba, K and Sr) and LREE (La, Ce) and prominent negative Nb, Ta, and Ti anomalies, all typical of subduction-related lavas. There is a systematic increase in the REE fractionation from calcalkaline (La_N/Yb_N: 4-5) to high-K calcalkaline (La_N/Yb_N: 6-10) to shoshonitic (La_N/Yb_N: 4-19) lavas.

The calcalkaline rocks from the northern and southern areas have similar ⁸⁷Sr/⁸⁶Sr_(i) (0.705764-0.706959) and ¹⁴³Nd/¹⁴⁴Nd_(i) (0.512402-0.512531) isotopic ratios. The shoshonitic rocks from the two areas, however, have different Sr-Nd isotopic systematics. The shoshonites from the southern area have relatively low ⁸⁷Sr/⁸⁶Sr_(i) (0.704541-0.705022) and high ¹⁴³Nd/¹⁴⁴Nd_(i) (0.512589-0.512797) ratios that are independent of SiO₂ content and plot near Bulk Earth in a Sr-Nd correlation diagram. The shoshonites from the northern area, however, have high ⁸⁷Sr/⁸⁶Sr_(i) (0.706664-0.708340) and low ¹⁴³Nd/¹⁴⁴Nd_(i) (0.512266-0.512364) ratios plotting in enriched mantle quadrant of a Sr-Nd correlation diagram (Figure 1). Furthermore, ⁸⁷Sr/⁸⁶Sr increases and ¹⁴³Nd/¹⁴⁴Nd decreases with increasing SiO₂ content, suggesting progressive contamination with crystal fractionation. Thus, crustal contamination appears to have played an important role in the genesis of the northern shoshonites and was responsible for their higher K contents, but contamination was apparently not involved in the genesis of the southern shoshonites. This suggests that crustal contamination is not essential for the genesis of shoshonitic volcanism.

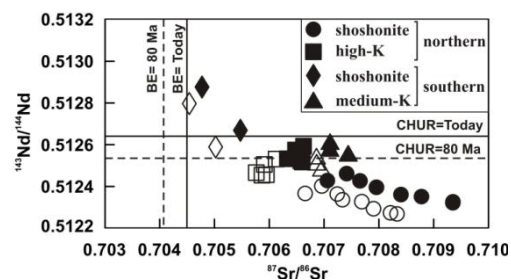


Figure 1: Sr-Nd correlation diagram of the volcanites (closed symbols: measured, open symbols: age corrected ratios for 80 Ma).