

Enhancement of Iron Solubility by Organic Matters in Sea Spray Aerosol

*Kohei Sakata¹, Minako Kurisu², Hiroshi Tanimoto¹, Aya Sakaguchi³, Yasuo Takeichi⁴, Yoshio Takahashi²

1. National Institute for Environmental Studies, 2. The Univ. of Tokyo, 3. Univ. of Tsukuba, 4. High Energy Accelerator Research Organization

Introduction: Fertilization of iron (Fe) in the ocean, followed by the promotion of primary production has great impacts on the Earth's climate (Martin et al., 1994; Jickells et al., 2005). Atmospheric deposition of mineral dust is considered as one of the important sources of dissolved Fe (dFe) in the surface ocean (Baker et al., 2016). However, factors controlling the solubility of Fe in aerosols are still under discussion. Water-soluble organic carbon (WSOC) was suggested to be one of the factors to increase the solubility of atmospheric Fe in the ocean (Baker et al., 2016). However, detailed processes of the increase of atmospheric Fe solubility by WSOC have not been clearly understood. In this study, we focus on external mixing of sea spray aerosol (SSA) and mineral dust because (i) dFe in the surface ocean is organic complexes (Rue and Bruland, 1995), (ii) the concentrations of Fe-ligands in the surface ocean are higher than dFe concentration (Buck et al., 2015), and (iii) submicron SSA enriches WSOC 10^3 to 10^5 times higher than the surface ocean (Quinn et al., 2015). It is expected that external mixing of organic ligands in SSA and Fe in mineral dust increases the atmospheric Fe solubility by formation of highly soluble Fe species. Therefore, we conducted macroscopic and nanoscopic X-ray speciation experiments of Fe in marine aerosols were conducted in order to understand a process of the enhancement of the Fe solubility by WSOC in SSA.

Methods: Size-fractionated sampling of marine aerosols were conducted during a research cruise of *R/V Hakuho-Maru* (KH-14-6, GEOTRACES, latitudinal cruise of the Western Pacific). Custom-built PTFE filters were employed because filter backgrounds of trace metals were 10^{-2} to 10^{-3} times lower in the custom-built PTFE filters than commercial cellulose filters. Trace metal concentrations were measured by inductively coupled plasma mass spectrometry (ICP-MS). Macroscopic Fe speciation experiments were conducted by X-ray absorption fine structure (XAFS) spectroscopy. In addition, Fe species and their mixing states in individual aerosol were determined by a nanoscopic speciation technique of scanning transmission X-ray microscope.

Results and Discussion: Total Fe concentrations in aerosols were higher in coarse fractions than in fine fractions. In contrast, the concentrations and extractabilities of labile Fe were higher in the fine fractions. The size-distributions of Fe extractability were similar to those of WSOC. These results indicated that the dissolution of Fe from aerosol particles were related with WSOC. Iron species in aerosol particles larger than $0.69 \mu\text{m}$ were typical crustal materials: biotite and Fe-(hydro)oxides. On the other hand, aerosol particles finer than $0.69 \mu\text{m}$ contained Fe(III)-organic complexes of citric acids and deferoxamine (DFO). Extraction experiments with Fe speciation showed that the spectrum of total Fe can be explained by insoluble Fe (residue of extraction) and Fe(III)-organic complexes. This result means that Fe(III)-organic complexes preferentially dissolved in the aqueous-phase. In addition, nanoscopic Fe speciation experiments revealed that Fe in mineral dust co-existed with OC and Na (tracer of SSA) on the aerosol surface. Citric acid and DFO are simulated materials of siderophore in the surface ocean (Barbeau, 2006). Therefore, siderophore-like organic matters from seawater play an important role in increasing atmospheric Fe solubility. Enhancement of the atmospheric Fe solubility by WSOC is important to regulate

the Earth' s climate not only in the present but also in the past because this process can be explained by only natural materials.

Keywords: Sea spray aerosol, Iron (Fe), Water soluble organic carbon, X-ray absorption fine structure, Scanning transmission X-ray microscope