Changes in iron species and iron solubility in Asian dust during the long-range transport from western China to Japan

Iron (Fe) is an essential micronutrient and has been identified as a limiting factor for the growth of phytoplankton in high-nitrate low-chlorophyll (HNLC) regions of the ocean [1]. In the North Pacific, one of the HNLC regions, transport and deposition of mineral dust from Asia can be one of the major sources of Fe. In the atmosphere, Fe can be found and transported in various chemical forms, both water-soluble and water-insoluble. It is generally believed that the soluble fraction of Fe is mainly considered as bioavailable for phytoplankton in the open ocean [2].

The overall solubility of atmospherically transported Fe at seawater pH is estimated to be 0.8–2.1%. However, large uncertainties exist in the estimates of bioavailable Fe deposited from the atmosphere, owing to a wide Fe solubility range in seawater. Although it has been suggested that atmospheric processes can change the solubility of Fe as it moves from the source region on land to the deposition area in oceans, actual chemical processes affecting Fe species in the solid phase in mineral dust are not clear. For example, photoreductive processes, in-cloud processes, and uptake of secondary acids can increase the solubility and bioavailability of Fe in dust particles. However, a change in Fe species during long-range transport based on actual data on the Fe species has not been widely studied up to now, which must be performed because the bioavailability of Fe is affected by its solubility, which in turn depends on the chemical species of Fe contained in Asian dust.

To accurately assess the biogeochemical impact of the atmospheric input, therefore, an attempt was made in this study to identify the Fe species and quantify each species by synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy, a powerful technique used to investigate chemical speciation in aerosol samples [3,4]. In addition, leaching experiments were conducted for natural Asian dust samples with complete information on Fe species contained in the dust, by which it was possible to show the relationship between Fe species and its solubility.

In this study, we focus on the speciation of Fe in mineral aerosols transported from Aksu (western China near Taklimakan Desert) to Qingdao (eastern China) and Tsukuba (Japan) [5]. By the fitting of the X-ray absorption near-edge structure (XANES; Fig. 1) and extended X-ray absorption fine structure (EXAFS; Fig. 2) measured in both fluorescence and electron yield modes at beamline **BL01B1**, it was revealed that Fe species changed from illite and chlorite (both are clay minerals frequently found at Earth's surface) originally contained in the dust in Aksu to illite and

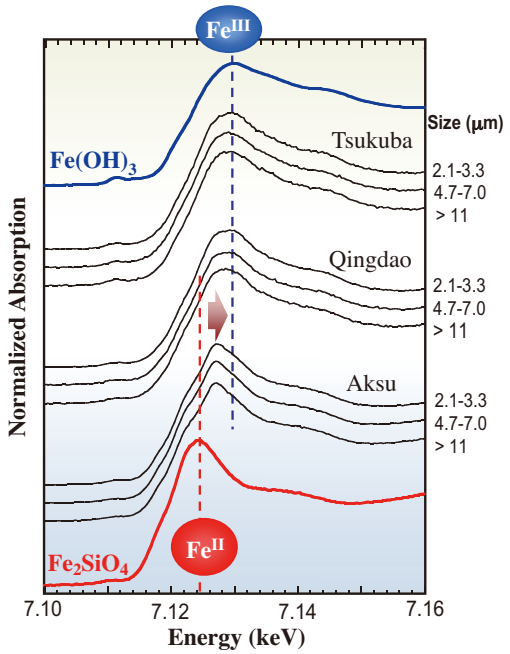

Fig. 1. XANES spectra of Fe in dust samples collected in Aksu (western China), Qingdao (eastern China), and Tsukuba (Japan) with reference materials Fe(II) and Fe(III). The shift in peak energy suggests the oxidation of iron during the long-range transport.

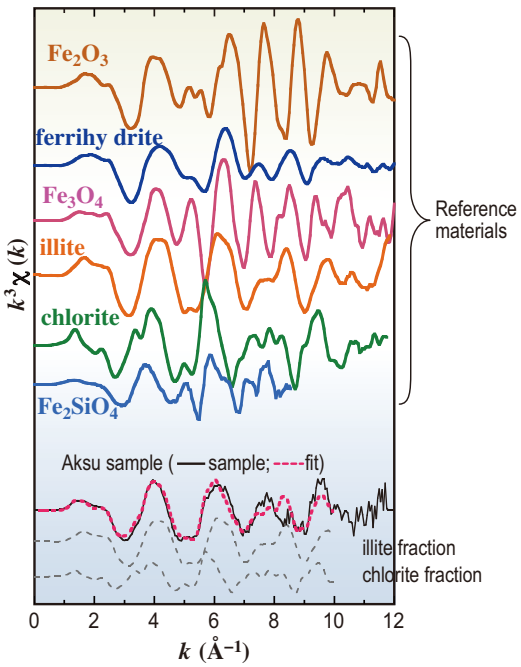

Fig. 2. Example of EXAFS fitting (k space) to estimate Fe species in dust sample collected at Aksu in western China.

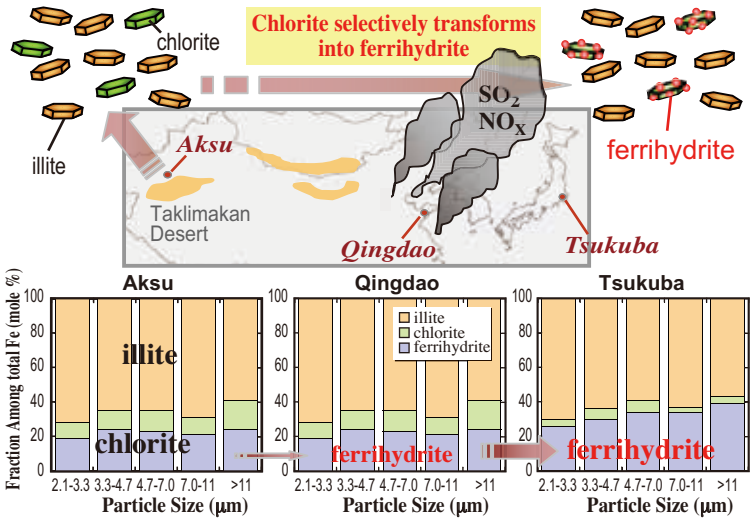

Fig. 3. Transformation of illite into ferrihydrite during the transport from western China to Japan.

ferrihydrite (amorphous iron hydroxides abundant at earth's surface) in Qingdao and Tsukuba (Figs. 1-3). The validity of the speciation determined by XANES and EXAFS was confirmed by X-ray diffraction and chemical extraction methods. The speciation showed that chlorite originally contained in the dust was selectively transformed into ferrihydrite during the long-range transport from Aksu to Qingdao and Tsukuba (Fig. 3). The high reactivity of chlorite compared with illite has been suggested in alteration experiments of the two minerals in mineralogical studies, which supports our results. Since the alteration of calcite to gypsum due to the reaction of calcite with sulfuric acid and also the enrichment of Pb in finer particles were found in Qingdao and Tsukuba for the same samples examined here [4], it is most likely that the transformation of chlorite to ferrihydrite is facilitated by anthropogenic effects (Fig. 3). Solubility experiments showed that Fe in ferrihydrite is more soluble than those in illite and chlorite. For natural samples, Fe in Tsukuba samples (main Fe host phases: illite and ferrihydrite) was more soluble than that in Aksu samples (illite and chlorite), as shown in Fig. 4. The results demonstrate that the transformation of chlorite to ferrihdyrite in aerosols during the long-range transport can increase the solubility of Fe in dust to seawater. In particular, it is strongly suggested that the dust passing through the highly populated and industrialized regions in eastern China has ample opportunity to be subject to the effects of pollutants, which can enhance the primary productivity and CO_2 uptake of the ocean, assuming that the anthropogenic emission of SO_2 and NO_X has some effects on Fe dissolution from mineral dust.

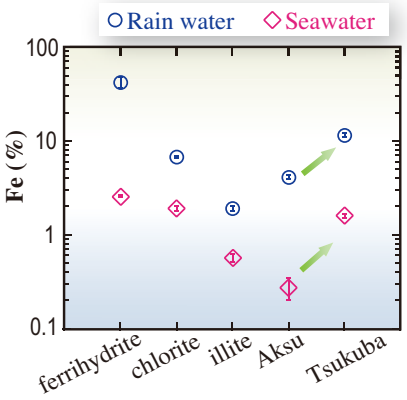

Fig. 4. Solubilities of Fe in simulated rainwater and seawater for standard minerals (illite, chlorite, and ferrihydrite) and aerosol samples collected in Aksu and Tsukuba.

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