

## Solubility of iron in aerosols of volcanic origin with iron speciation analysis

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In high nutrient low chlorophyll (HNLC) region, which covers 20% of the world oceans, growth of phytoplankton is limited by iron (Fe) concentration (Martin and Fitzwater, 1988). It has been suggested that aerosols can be an important supply source of Fe to the HNLC region. The solubility in ocean of Fe in aerosols, in turn, depends on its chemical species, but the Fe species in the aerosols have not been fully clarified. Therefore, the aim of this study is to determine the Fe chemical species and its solubility in aerosols of various sources. In particular, there have been few studies on the Fe speciation and solubility in aerosols of volcanic origin. Thus, marine aerosol samples of volcanic origin were examined in this study. The aerosol samples were collected from the Northwestern Pacific during research cruise of Hakuho-Maru (KH-08-2) in summer in 2008. As a result of backward trajectory analysis for the sample (Leg.1-5) when high sulfate concentration was detected, it was suggested that the aerosol samples was supplied from the Okmok volcano in the Aleutian Islands of Alaska as volcanic ashes. Hence, the volcanic ashes (< 20, 20-32, and 32-250 micron) of Okmok volcano received from Alaska Volcano Observatory were also studied as well as yellow dusts (CJ-1, CJ-2, and Gobi Kosa Dust) for comparison.

The Fe/Al ratio in the Leg.1-5 sample was identical to that of the volcanic ash sample, showing that the aerosols collected during the Leg.1-5 is supplied from the eruption of the Okmok volcano, which reinforces the suggestion by the backward trajectory analysis. Sulfur K-edge XANES showed that sulfide originally contained in the volcanic ash changed into sulfate possibly due to the alteration during the transport to the Northwestern Pacific. Iron K-edge XANES analysis showed Leg.1-5 contained ferrihydrite (60%), magnetite (28%), and iron(II) sulfate (12%), whereas volcanic ashes (< 20 micron) contained augite (57%), fayalite (25%), and pyrite (18%). CJ-1 and CJ-2 contained illite, ferrihydrite, and chlorite, while Gobi Kosa Dust contained illite, ferrihydrite, and hematite. In addition, the average valence of Fe determined by pre-edge fitting of Fe K-edge XANES showed that the ratio of ferric iron of Leg.1-5 (average valence of Fe = 2.4) is higher than that of volcanic ashes (average valence of Fe = 2.1). These results showed aerosols of volcanic origin released into the atmosphere were altered and oxidized while being transported.

The total Fe concentration (T-Fe) in samples after acid decomposition and the dissolved Fe concentration (D-Fe) in samples extracted by MQ water or simulated seawater (pH 8) were determined by ICP-AES. The Fe solubility ( $Fe_s$ ) here was defined as the percentage of Fe released in the solution after 24 h:  $Fe_s (\%) = (D-Fe/T-Fe) \times 100$ . The results showed that the solubility to seawater ( $Fe_s$ -SW) of Fe contained in the aerosol samples of volcanic origin is larger than that of yellow dusts by a factor of more than 1000. Generally speaking, Fe solubility depends on the valence of Fe, that is, the solubility decrease with the increase in the ratio of ferric iron for ferrous iron. In this study, however, the Fe solubility of the aerosol samples is higher than that of volcanic ashes mainly due to the formation of iron(II) sulfate, highly soluble species, as shown in the XAFS spectra. This is why volcanic ashes which originally contained insoluble Fe changed into the aerosols with high soluble Fe content.

Although the average emission of fine volcanic ash (176-256 Tg/yr; Durant et al., 2010) into the atmosphere is less than that of annual terrigenous dust load (1000-3000 Tg/yr; Tegen and Schepanski, 2009) by a factor of 1/10, the soluble Fe content in the aerosols supplied as volcanic ashes cannot be underestimated due to the very high soluble Fe content in the aerosols of volcanic origin.

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