CCN efficiency spectra of urban aerosol particles segregated by their hygroscopicities

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Cloud condensation nuclei (CCN) efficiency spectrum, i.e., the number fraction of CCN as a function of particle diameter, is a measure of the CCN activity of atmospheric aerosol particles. Here we applied the CCN efficiency spectra to urban aerosol particles segregated by their hygroscopic growth factors (HGF), using a CCN counter coupled to a hygroscopic tandem differential mobility analyzer (HTDMA). The investigation was performed for 10 days in the city of Nagoya, Japan, in June 2008. Atmospheric aerosol particles were first classified according to their dry diameters and then classified according to their HGFs at 85% RH. The fraction of CCN in the classified particles was measured at water vapor supersaturations (SS) of 0.21%, 0.36%, and 0.82% using the CCN counter. To obtain the CCN efficiency spectra for particles with different HGFs, the diameter of particles classified in the first DMA was scanned, while the ratio of the diameters of particles classified in the second DMA to those of the first DMA was adjusted to 1.00, 1.18, and 1.36.

From the CCN efficiency spectra of HGF-segregated particles, the diameters at which the CCN efficiency increased to 50 % of the maximum efficiency (d_{50}) were calculated from a curve fitting with a cumulative log-normal function. While the observed temporal variation of d_{50} was small under the conditions of same SS and HGF, the d_{50} values decreased with increasing HGF at fixed SS, and they decreased with increasing SS at fixed HGF. For particles classified at HGF=1.18 and 1.36, the d_{50} values were close to the theoretical activation diameters predicted by the Köhler theory. In contrast, the d_{50} values of particles classified at HGF=1.00 were much smaller than the activation diameters predicted for a hypothetical sphere particle without solute but wettable with pure water. The large difference between the observed d_{50} and theoretical activation diameters indicates that water-soluble materials in less hygroscopic particles strongly enhance their CCN activity in the urban atmosphere. Further, diurnal variation of the maximum value of the CCN efficiency was observed for particles classified at HGF=1.00. Change in the chemical composition of particles during photochemical aging is a possible cause of the variation.

Iron isotopic distribution at grain scale sugggests the redox fluctuation of the Archaean shallow ocean

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The secular evolution of the redox status of the shallow ocean has probably strongly influenced the material cycle [1, 2] and evolution of the photosynthesis-based ecosystem, including O_2-producing cyanobacteria. Iron is a redox-sensitive element, which exists as a soluble Fe(II) species or insoluble Fe(III) species on the Earth's surface. In contrast to the Fe(II)-free modern oxic ocean, dissolved Fe(II) is considered to be much more abundant in the Archaean ancient ocean (4.0 ~ 2.5 Gyr ago). Although the iron isotopic ratio of marine sedimentary minerals has the potential to provide key information on the marine redox state [3,4], a quantitative estimate of the redox state of the Archaean shallow ocean is highly restricted. This is because the iron isotopic record may be obscured by homogenization of isotopically distinct components within the same rock, if we use the conventional bulk isotope analytical technique. Here we report an *in situ* iron isotopic ratio of individual pyrite grains in stromatolitic carbonates over geological time, using a newly developed femtosecond laser ablation multi-collector ICP-MS technique (fs-LA-MC-ICP-MS). We have first discovered that the grain-scale iron isotopic distribution of pyrite from the coeval samples always shows a bimodal or unimodal pattern. Further, the bimodal pattern is often observed in a single rock specimen. The discrete iron isotopic patterns are well explained in a framework of an Fe(II) steady state model in the shallow ocean; thus the data allow us to estimate the degree of Fe(II) oxidation in the Archaean shallow ocean. Estimated values of oxidized fractions of the Fe(II) influx in the shallow ocean at 2.9, 2.7 and 2.6 Gyrs suggest that the redox potential of the Archaean shallow ocean has not increased monotonically, but has fluctuated through geological time.

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