Nitrogen and oxygen isotopic composition of atmospheric nitrate near the highways

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Nitrogen isotope ratio ($\delta^{15}N$) and conventional oxygen isotope ratio ($\delta^{18}O$) in atmospheric nitrate has been used to estimate the NO_X sources and its oxidation pathways. Recently, ^{17}O-excess ($\Delta^{17}O \approx \delta^{17}O - 0.52 \times \delta^{18}O$) is known to be more robust indicator of atmosperic nitrate formation pathways than $\delta^{18}O$ value. Although the $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$ values in atmospheric nitrate have been studied in various regions [e.g. ref.1 and references therein], only a few observations of the oxygen isotope ratios in urban area have been reported. In this study, we collected precipitation and atmospheric particles near the highways located in Yokohama, Japan from Janualy 2012 to December 2012, and measured $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$ values in nitrate.

Precipitation samples were collected using a funnel and plastic bottle. The atmospheric particle samples were collected on quartz filters using high-volume air sampler. The filters were replaced every week. The stable isotope ratios of nitrate were measuerd by GC-IRMS after converting nitrate to N_2O.

The $\delta^{15}N$ and $\delta^{18}O$ values in precipitation, and the $\delta^{15}N$ values in particle showed a temporal variation similar to the previously reported values (-2.2‰ < $\delta^{15}N$ < 13.6‰ and 52.6‰ < $\delta^{18}O$ < 83.4‰) [2, 3]. The variation of $\delta^{18}O$ values in particulate nitrate was similar to that of precipitation, but extremely low values (26.2‰ to 39.7‰) were observed from the end of August to the end of November. The low $\delta^{18}O$ values cannot be explained by typical nitrate formation processes that involve ozone, and imply that isotopically light oxygen, such as O_2 ($\delta^{18}O$ = 23.5‰) played a key role in NO_X oxidation prosess in the period [4, 5]. Implication from $\Delta^{17}O$ data will be also discussed.

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Anoxic geothermal fields and the early life

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We have reconstructed the 'hatcheries' of the first cells by combining geochemical analysis with phylogenomic scrutiny of the inorganic ion requirements of universal components of modern cells [1]. These ubiquitous, and by inference primordial, proteins and functional systems show affinity to and functional requirement for K^+, Zn^{2+}, Mn^{2+}, and phosphate. Thus, protocells must have evolved in habitats with a high K^+/Na^+ ratio and relatively high concentrations of Zn, Mn and phosphorous compounds. Geochemical reconstruction shows that the ionic composition conducive to the origin of cells could not have existed in marine settings but is compatible with emissions of vapor-dominated zones of inland geothermal systems. Under anoxic, CO_2-dominated atmosphere, the elementary composition of pools of condensed vapor at anoxic geothermal fields would resemble the internal milieu of modern cells.

The scientists who address the origin of life problem from a purely chemical viewpoint argue that specific formation of activated, cyclic ribonucleotides with a potential for polymerization could take place in formamide-rich solutions, particularly under the action of UV light and in the presence of borate and phosphorous compounds [2, 3].

The exhalations of even modern geothermal fields contain high amounts of ammonia, phosphate, borate and hydrocarbons, so that the anoxic geothermal fields should have been conducive for formation of simple amides and nitrogen-containing organic molecules, including activated nucleotides.

Hence, the anoxic geothermal fields, which we identified as tentative cradles of life by using the top-down approach and phylogenomic analysis, could provide exactly those geochemical conditions that were suggested as most conducive for the emergence of life by the chemists who pursued the complementary bottom-up strategy.

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