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## Stepwise combustion analyses of distinct nitrogen isotopic compositions on Paleoproterozoic organic matter

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Nitrogen isotopic compositions (= $d^{15}N$ ) of organic matter in the sedimentary rocks are recognized as an indicator for the redox condition of the ocean and microbial activity during an ancient age. The changes of  $d^{15}N$  values of kerogens indicate that the change of global nitrogen cycle associated with aerobic nitrogen cycling including nitrification and denitrification. These processes result the loss of  $^{14}N$  to the atmosphere, and make the nitrogen fixed into the organic  $^{15}N$ -rich.

However, the heterogeneity of nitrogen isotopic compositions in kerogens, which could indicate the difference of microbial species, forms and degree of metamorphic effects, was less understood in the previous studies. The stepwise combustion method is one of the effective tools to detect heterogeneity of nitrogen isotopic compositions in kerogens. However, there still remain many unsolved problems to apply this method to analyses of Precambrian organic matter.

Nitrogen isotopic analyses were conducted on two kerogen samples from the Gunflint Formation (ca. 1.9 Ga) using the stepwise combustion technique to evaluate a potential analytical problem for the carbonaceous samples and to assess if this method is appropriate for the analysis of ancient rocks. As a result, we were able to confirm two well discriminated  $d^{15}N$  plateaux in a single organic matter, with mean value of +5.0 permil and +7.3 permil on sample 0708, and with mean value of +6.1 permil and +5.2 permil on sample 0704. The direction of the  $d^{15}N$  shift is opposite in each sample.

This characteristic excludes the possibility of analytical artifact as the source of isotope fractionation and metamorphism isotope fractionation. The two distinct  $d^{15}N$  values observed for each of the samples are characterized by different activation energies for the co-released carbon. These results suggest that similarly aged sedimentary rocks may contain at least two types of organic matter that record different source information for  $d^{15}N$ .

Keywords: stepwise combustion method, nitrogen isotopic composition, kerogen, Paleoproterozoic, Gunflint formation