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A new approach for detecting trace elements in microfossils: implications for the Paleoproterozoic biosphere

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We developed a novel procedure to detect trace elements left in the Paleoproterozoic 'Gunflint microfossils' using lateral high-resolution secondary ion mass spectrometry (NanoSIMS). The Gunflint microfossil has been studied and used as a 'reference material' for microfossil research. Although their microscale analyses of major organic elements (N, C, S) have been performed, bioessential trace elements that have crucial information to determine not only metabolic pathways but also implicate the elemental cycle in the biosphere at that time, have rarely been measured because of several technical difficulties.

In this study, we improved the previous acid treatment technic, and succeed to isolate Gunflint microfossils from bulk chert rock keeping their original form. Isolated samples were mounted on conductive glass for optical and electron microscopic observations. By these treatments, higher secondary ion yield than a thin section sample was achieved because the matrix was physically removed. As a result, we succeed to detect trace amounts of phosphorus (P) and molybdenum (Mo) directly from the organic part of the filament-type microfossil. Detection of organic P from the Paleoproterozoic Gunflint microfossils, which is the first report, suggests that microbes at that time had already utilized P and evolved P-based biostructures and functions such as phospholipid membrane or ATP. In addition, detection of organic-related Mo from microfossils, which is the typical central metal of nitrogenase, is consistent with the morphological and isotopic prediction that this type of microfossil is cyanobacteria. This implies the increased availability of molybdenum due to the expanding continental oxidative weathering and shows that the global nitrogen cycle was functioning by cyanobacterial fixation at this age. Our procedure of in situ trace element analysis is potential to be used as a new biomarker for microfossil research and prescribe origin and evolution of biosphere through Precambrian eon.