The early evolution of the Archean nitrogen biogeochemical cycle

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Nitrogen constitutes essential biomolecules (e.g., nucleic acids, amino acids, and proteins) for sustaining life. The present-day marine N cycle is characterized by a series of oxidation – reduction reactions (e.g., N_2-fixation, nitrification, and denitrification). These reactions are mediated by a variety of organisms. Gene sequencing revealed that the biological N_2-fixation has its deep root into the “tree of life”.

To assess the timing of the onset of such processes of N (redox-) cycling in the Earth's history, we determined stable isotopic compositions and contents of organic-N, inorganic-N (clay-N), and organic C of 3.25 - 2.22 billion-year old carbonaceous sedimentary rocks. We analyzed >60 samples of mainly shales from 6 Groups collected in South Africa and Australia, and compared with Phanerozoic shales of various ages.

The distribution pattern and magnitude of N isotopic compositions of the 3.25 Ga black shales and the other Archean–Paleoproterozoic samples are found to be very similar to those of Cretaceous black shales. The N isotopic compositions of organic-N are close to 0 ‰ and those of inorganic-N are positive (~+4 ‰).

As common mechanisms that have controlled marine biogeochemical cycling of N since at least 3.25 billion years ago, we suggest not-mutually-exclusive two mechanisms. One is the microbially mediated redox-cycling of N, involving (possibly cyanobacterial) N_2-fixation from the atmosphere and denitrification-nitrification in the ancient sedimentary environments. The other mechanism is the microbially mediated non-redox cycling of NH_4^+ between organisms and clays in the ancient sediments. In either case, this study suggests the operation of the microbial N cycling at least since the Mesoarchean. The results of this study are supported by the different data set for other Archean-Paleoproterozoic black shales in Australia (Naraoka *et al.*, in prep).

This study has important implications for the redox evolution of atmosphere and oceans and for the early evolution of the present-day style marine biogeochemical cycling of N.

A HREE-enriched biogenic ferric redox band in tuffaceous sedimentary rock

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The focus of this study is a redox front generated from a fracture surface in Tertiary tuffaceous sedimentary rock occurring in central Japan. The geological setting and features of the redox front’s spatial distribution pattern show that redox reactions have progressed within approximately the last several hundreds of ka, following development of the Quaternary cover’s present surface topography. In the sample investigated, the redox band had a width of 17cm and was cut into 17 pieces along the fracture surface. These pieces were analysed by XRF for major and trace elements and by ICP-MS for REEs, to understand the elemental profile from the fracture to the rock matrix. Also, direct examinations with EPMA and SEM-EDS have been carried out to characterise the spatial distribution of elements as well as the microscopic geochemical nature of the front.

The XRF analysis showed that Mn is concentrated in three sharp layers, situated near the fracture surface (less than 20mm). In contrast, the most Fe-concentrated layer was seen from about 50mm from the surface. This strongly suggests that fractionation between Mn and Fe has occurred during front migration. The Mn-concentrated layers also show enrichments of various trace elements such as Zn, Co, Ni, and Ba. On the other hand, the Fe-concentrated layer is characterized by enrichments of P and heavy REEs. The EPMA showed the Fe is distributed heterogeneously in the band and necessarily accompanies P high enrichment. Detailed SEM observation revealed that a fossil microbe colony occurs in the pore space. In places microbial mats with bacterial cells were also identified. Direct examination of the microbial mats with SEM-EDS showed that they are composed of amorphous granules made exclusively of Fe and Si. This suggests that the bacterial activity played an important role in the concentration and fixation of Fe in the redox band under low temperature conditions. Additionally, it is conceivable that the heavy REE enrichment also progressed at the same time. Mass balance calculations were done using the REE analyses of the redox band and the present formation water. If the band formed in the presence of groundwater like that occurring presently, about 10^6 pore-volumes of water would have been required to form the excess REE concentrations in the band.

The implications of these long-term enrichment and fixation processes by biogenic redox front generation at low temperatures will be explored. These implications are relevant to understanding, for example, elemental migration in the global surface weathering system and/or long-term heavy metal fixation for pollutant remediation.