

Chemical and isotopic characteristics of biogenic elements in late Archean shales

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Archean biological activity must have played an important role in the early evolution of Earth's surface environments, including CO₂ and O₂ contents of the atmosphere and oceans. Recent discovery of molecular fossils of cyanobacteria and eukaryotes from late Archean sediments indicates the prevailing of O₂-producing photosynthesis by ~2.7 Ga. Some molecular and carbon isotope studies also support the development of complex bacterial ecosystems in late Archean ocean. On the contrary, a large sulfur-mass independent fractionation (S-MIF) was also reported from late Archean sediments, which invoke a different sulfur cycle (mainly operated by photochemical reactions) from modern surface environment. Therefore, chemical and isotopic signature of late Archean sediments could be critical to study the evolution of biosphere and biogeochemical cycle of the Earth.

In this paper, we will report chemical and isotopic characteristics of the Mount McRae Shale (~2.55 Ga) from the Hamersley district, which immediately underlies the Brockman Iron Formation. Through the ~22 m drilling core section, the shale is extremely rich in organic carbon (up to ~10 wt%) and pyrite (up to ~5 wt% as sulfur). Organic carbon content is positively correlated with nitrogen (N) and sulfur (S), suggesting the N and S are also biogenic. The original d¹³C values of organic matter, estimated from the d¹³C values and H/C of kerogen, changed from -35 to -39 per mill (vs. PDB). Bulk d³⁴S varied from ~ -7 to ~ +12 per mill (vs. CDT), suggesting that the maximum isotopic fractionation between sulfate and sulfide could be ~20 per mill. A distinct positive correlation is found between the d³⁴S and d¹³C values of kerogen. Pyrite with high d³⁴S values (+7 to +12 per mill) occur with kerogen with high d¹³C values (~-35 per mill), while pyrite with low d³⁴S values (-7 to +1 per mill) occur with kerogen with low d¹³C values (~-39 per mill). Coupled with the sulfur content and d³⁴S distribution, the organic d¹³C variation may be caused by a mixing of at least two different organic matter derived from oxygenic photosynthesis (i.e. cyanobacteria) and CH₄-assimilated bacteria. Bulk nitrogen content varied from 0.06 to 0.15 wt% with N/organic C atomic ratio of 0.013 to 0.033, and the N/C of kerogen ranges from 0.0044 to 0.0085. Therefore, the biogenic N in the shales mostly (~60%) resides in clays, rather than in kerogen. Bulk d¹⁵N ranged from +2 to +7 per mill (vs. Air), which is the same range as the d¹⁵N of modern ocean. However, kerogen was depleted in ¹⁵N by ~4 per mill relative to bulk nitrogen. The Mo concentration ranges from 2 to 17 ppm, being more enriched from the crustal average (~1 to 2 ppm), which positively correlated with organic C content. Weathering of crustal Mo under oxidative condition and the fixation of Mo with organic C under reducing condition could be operated in the basin.

These chemical and isotope variations such as d¹³C fluctuation (-39 to -35 per mill), positive d¹⁵N (+2 to +7 per mill), abundant pyrite S with the maximum isotope fractionation of ~20 per mill, and the Mo enrichment (up to 17 ppm) correlated with organic C content, probably suggest that the ocean in the ~2.55 Ga Hamersley Basin had fluctuated its redox condition.