Stability of Kerogen in 3.2 Ga Black Shales during Thermal Alteration Experiments: Implications for its Origin.

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Introduction: Organic matter retained in Archean rocks has extremely important information for investigating the evolution of microbial biosphere in the early Earth. Current studies suggest that eukaryote first appeared on Earth ~2.1 Ga [1], or possibly at least ~2.7 Ga [2]. However, accumulating evidence suggests that microbial biosphere was already diverse at least by 3.2 Ga ago [e.g., 3]. To reveal the origin of organic matter preserved in the 3.2 Ga old black shales recovered by continental drilling in 2007 called DXCL-DP [4, 5], extracted kerogen was spectroscopically analyzed utilizing micro FT-IR spectroscopy and laser Raman microspectroscopy. Thermal alteration experiments were also performed in order to investigate the chemical stability of kerogen which underwent variable degrees of thermal overprints.

Analytical Methods: FT-IR and Raman spectroscopic analyses were performed at Kochi University. Using the Raman spectrum, we determined the central wavenumber of D and G bands and corresponding full width at half maximum (FWHM). Using the IR spectrum, we determined the value of $R_{3/2}$, the ratio of peak heights for the asymmetric stretching vibration of the CH_3 and the CH_2 groups of aliphatic hydrocarbons. This ratio may be used as a proxy to determine the origin of kerogen either bacteria, archea, or eukarya [6].

Thermal alteration experiments were performed at different temperatures (300, 350 and 400˚C) mimicking thermal alteration and at various duration (8 hours, 1, 3, 5 and 7 days) using an electric furnace (dry condition; not mimicking hydrothermal alteration).

Results: The Raman spectra of untreated kerogen samples were almost uniform and have relatively broad FWHM of D and G bands among them, suggesting that the samples were subject to only weak thermal metamorphism. Almost identical positions of central wavenumber of the D and G bands among the samples with different drilling depths suggest that such metamorphism evenly affected the unit. Based on a previous study suggesting utility of $R_{3/2}$ ratios as a mean to classify the origin of organic matter into three types (eukarya, bacteria, and archea [6]), the $R_{3/2}$ ratios of our samples indicate that bacteria and eukarya are the likely origin of organic matter (later converted to kerogen) in the 3.2 Ga black shales [7].

Eukarya in 3.2 Ga ocean?: Involvement of eukarya as an origin of kerogen in the 3.2 Ga black shales, if true, has far-reaching implications for the evolution of microbial biosphere in the early Earth. However, there remains possibility that the $R_{3/2}$ ratios of our samples are actually an artifact of post-depositional alterations. To examine such possibility, we conducted thermal alteration experiment to see if artificially altered kerogen changed its $R_{3/2}$ ratio depending on alteration temperature and duration.

Thermal Alteration Experimetns: Changes were indeed observed of the central wavenumbers of D and G bands and the FWHM in the Raman spectra and the $R_{3/2}$ ratios calculated from the IR spectra, when the kerogen was heated up to 400˚C. The FWHM and $R_{3/2}$ ratios showed changes at lower temperature, 350˚C. These results suggest that organic matter in the 3.2 Ga black shales has undergone minimal thermal alteration at <350˚C, fully consistent with lower greenschist metamorphic grade of the entire unit. These results further suggest that our original suggestion of eukaryotes as a source of organic matter in the 3.2 Ga black shales was robust; the $R_{3/2}$ ratios indicating eukaryotes was not an artifact of post-depositional alteration.

Implications: This study has important implications for the evolution of microbial biosphere in the Archean, especially the emergence of eukaryotes.

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