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# Biomarker mapping by MALDI-TOFMS: Implications for indigenous 2-methylhopane for oxygenic photosynthesis preserved in the Archean and Proterozoic black shales

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Authenticity of 2 alpha-methylhopane, a likely biomarker of oxygenic photosynthesizers cyanobacteria, extracted from the 2.7 Ga black shale ([1], [2]) has also been challenged ([3], [4]). The timing of emergence for oxygenic photosynthesis remains unconstrained. It is important to determine if a “biomarker” in black shales is indigenous or contamination in later stages by a novel method.

Here we report the results of *in situ* biomarker mapping, by MALDI-TOFMS or imaging mass spectrometry, for Archean-Paleoproterozoic black shales from Australia and Ghana. The MALDI-TOFMS method has advantages over the traditional GC-MS method, where location information is lost during biomarker extraction from rocks that are powdered and homogenized for extraction by organic solvents.

We could observe 2D, sedimentary-structure-dependent distributions of hopane in thin sections made from drillcores of the black shales in the 3.2 Ga and 2.7 Ga black shales from Pilbara, Western Australia, and 2.2 Ga black shales from Ghana. The 2.7 Ga drillcores were used for detection of 2 alpha-methylhopane by [1] and for geochemical and isotopic analyses by [5]. We also used drillcores (ABDP#10) of the shallow-facies stromatolitic carbonates of the 2.7 Ga Tumbiana Formation from the same district.

We confirmed syngenesity of hopane in all of the 3.2 Ga, 2.7 Ga, and 2.2 Ga black shales, suggesting operation of oxygenic photosynthesis in the shallow ocean well before and after the inferred GOE. Biomarker mapping by MALDI-TOFMS proved to be a powerful tool for testing its syngenesity. Our results have important implications for the evolution of microbial biosphere and that of redox states in the atmosphere-ocean system in the early Earth.

[1] Brocks et al. (1999) Science 286, 1033-1036. [2] Eigenbrode and Freeman (2006) PNAS 103, 15759–15764. [3] Brocks (2011) GCA 75, 3196-3213. [4] Rasmussen et al. (2008) Nature 455, 1101-1104. [5] Yamaguchi (2002) Ph.D. dissertation, Pennsylvania State University.