Spatially resolved, in situ carbon isotope analysis of Archean organic matter

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Spatiotemporal variability in the carbon isotope composition of sedimentary organic matter (OM) preserves information about the evolution of the biosphere and of the exogenic carbon cycle. Primary compositions, and imprints of the post-depositional processes that obscure them, exist at the scale of individual sedimentary grains (mm to μm). Secondary ion mass spectrometry (SIMS) (1) enables analysis at these scales and in petrographic context, (2) permits morphological and compositional characterization of the analyte and associated minerals prior to isotopic analysis, and (3) reveals patterns of variability masked by bulk techniques. Here we present new methods for in situ organic carbon isotope analysis with sub-permil precision and spatial resolution to 1 μm using SIMS, as well as new data acquired from a suite of Archean rocks.

Three analytical protocols were developed for the CAMECA ims1280 at WiscSIMS to analyze domains of varying size and carbon concentration. Average reproducibility (at 2SD) using 6 μm and 1 μm spot sizes with two Faraday cup detectors was 0.4‰ and 0.7‰, respectively, and 0.8‰ using a 3 μm spot with a Faraday cup (for ^{12}C) and an electron multiplier (for ^{13}C). Eight coals, two ambers, a shungite, and a graphite were evaluated for μm-scale isotopic heterogeneity, and LCNN anthracite ($\delta^{13}C = -23.56 \pm 0.10$‰, 2SD) was chosen as the working standard. The correlation between instrumental bias and H/C was calibrated for each analytical session using organic materials with H/C between 0.1 and 1.5 (atomic), allowing a correction based upon a $^{13}CH/^{13}C$ measurement included in every analysis. Matrix effects of variable C/SiO_2 were evaluated by measuring mm to sub-μm graphite domains in quartzite from Bogala mine, Sri Lanka. Apparent instrumental bias and ^{12}C count rate are correlated in this case, but this may be related to a crystal orientation effect in graphite. Analyses of amorphous Archean OM suggest that instrumental bias is consistent for ^{12}C count rates as low as 10% relative to anthracite.

Samples from the ABDP-9 core (n=3; Mount McRae Shale, ~2.5 Ga), RHDH2a core (n=2; Carrawine Dolomite and Jeerinah Shale, ~2.6 Ga), WRL1 core (n=3; Wittenoom Dolomite, Marra Mamba Iron Formation, and Jeerinah Shale, ~2.6 Ga), and SV1 core (n=1; Tumbiana Fm, ~2.7 Ga), each previously analyzed for bulk organic carbon isotope composition, yielded 100 new, in situ data from Neoarchean sedimentary OM. In these samples, $\delta^{13}C$ varies between –53.1 and –28.3‰ and offsets between in situ and bulk compositions range from –8.3 to 18.8‰. In some cases, isotopic composition and mode of occurrence (e.g. morphology and mineral associations) are statistically correlated, enabling the identification of distinct reservoirs of OM. Our results support previous evidence for gradients of oxidation with depth in Neoarchean environments driven by photosynthesis and methane metabolism. The relevance of these findings to questions of bio- and syngenicity as well as the alteration history of previously reported Archean OM will be discussed.