

Simultaneous in situ analysis of C and N Isotope ratios in organic matter by SIMS: application for geological samples

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An in-situ analytical method for simultaneous analysis of carbon and nitrogen isotope ratios ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) in organic matter was developed for $\sim 12 \mu\text{m}$ spots by secondary ion mass spectrometry (IMS 1280 at WiscSIMS). Secondary ions of $^{12}\text{C}_2^-$, $^{12}\text{C}^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$, and $^{12}\text{C}^{15}\text{N}^-$ are simultaneously measured by three Faraday cups and one electron multiplier. Ions of $^{12}\text{C}_2\text{H}^-$ were measured separately to monitor hydride interferences. Mass resolution power up to 8000 was achieved to resolve possible neighbor ions adjoining the objective ions. Five anthracite and one shungite were measured as a reference material to examine mass biases and isotope homogeneity. The spot-by-spot reproducibility of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of UWLA-1 anthracite (95.7 wt%C and 1.2 wt%N), which is the most homogeneous reference material, were 0.16‰ and 0.56‰ (2SD), respectively. A negative correlation was observed between the mass bias of carbon isotope ratio and $^{12}\text{C}_2\text{H}^-/^{12}\text{C}_2^-$ ratios of examined reference materials. In contrast, there is no correlation for nitrogen isotope measurements, suggesting the mass bias of nitrogen can be determined independently of the hydrogen. The mass bias corrected $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of reference materials were consistent with those results of bulk conventional analysis.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of 22 individual globules of organic matter in a carbonate rock from the 1.9 Ga Gunflint Formation, determined by the new procedure, were ranging -33.8 to -33.3 ‰ and $+4.2$ to 5.8 ‰, respectively. Mean values of them were consistent with bulk kerogen analysis within analytical precisions.

The ionization efficiency of $^{12}\text{C}_2^-$ ions in carbonate is significantly lower than that of reduced organic matter. The difference in carbon bonding between these materials would be responsible for this difference (i.e., C-O and C-C). This suggests that measurement of $^{12}\text{C}_2^-$ ions is highly advantageous for micrometre scale organic matter in a carbonate matrix.

Simultaneous analyses of carbon and nitrogen in the same nano-volume of organic matter in Precambrian sedimentary rocks will allow correlations with textures and mineralogical occurrences, which will provide more detailed constraints on environments and life on the early Earth. Furthermore, this method is applicability to research in modern biological studies such as: using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ as a proxy of modern or ancient food chains; fossil-based study of paleo ecosystems; and paleoclimatology targeting organic matter in marine biocarbonates. This work will help to expand the range of analytical tools available for the study of stable isotopes as a biosignature.

Keywords: secondary ion mass spectrometry, nitrogen isotope, carbon isotope, geobiology, micro scale