Acid treatment biasing to C/N, $\delta^{13}C$ and $\delta^{15}N$ of organic matter: A Molecular insight

Brodie, C.R.,[a] Leng, M.J.,[b,d] Casford, J.S.L.,[c]Heaton, T.H.E.,[d]Kendrick, C.K.,[d] Lloyd, J.M.,[c] Zong, Y.Q.,[a] and Bird, M.I.[e]

[a]Department of Earth Sciences, The University of Hong Kong, Pok Fu Lam Road, Hong Kong SAR
[b]*Department of Geology, University of Leicester, University Road, Leicester, UK*
[c]*Department of Geography, Durham University, Durham, UK*
[d]*NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, UK*
[e]*Earth and Environmental Sciences, James Cook University, Cairns Campus, Australia*

It is known that acid treatment methods employed to remove inorganic carbon (IC) from sample material prior to analysis for C/N, $\delta^{13}C$ and $\delta^{15}N$ cause non-linear, unpredictable biasing to the organic matter (OM) fraction. Consequently, measured C/N, $\delta^{13}C$ and $\delta^{15}N$ have an uncertainty much greater than instrument precision: uncertainties for C/N are reported in the range of 1 – 100, for $\delta^{13}C$ in the range of 0.2 – 6.8 ‰ and for $\delta^{15}N$ in the range of 0.2 – 1.5 ‰, in both modern and palaeo environmental materials. Brodie et al (2011) extended this investigation to a down-core lake sedimentary archive (Lake Tianyang, South China) and noted the potential for uncertainties to preclude "common" interpretations of the data (e.g., C/N values as an OM provenance tool; $\delta^{13}C$ as a proxy for changes in C_3 and C_4 vegetation). It is evident that the size of uncertainty between sample horizons varies considerably implying a differential relative reaction to acid treatment down-core (i.e., as the type, relative amount and physical state of organic and inorganic components change).

We are now investigating this biasing at the molecular level by employing ^{13}C-NMR and GC-IRMS techniques on a suite of modern and palaeo environmental materials and on a lake sedimentary archive. This will provide an important insight into the effect of acid treatment on organic compounds (i.e. removal from the sample, breakdown of compounds and partial removal) and associated isotopic fractionation. From an improved understanding of the type of compounds most susceptible to alteration/removal during the acid treatment processes it will be possible to consider refinements to the acid pre-treatment process and provide information on the relative down-core changes in those compounds susceptible to change (which we may be able to glean environmental information from).

Keywords: Acid treatment; C/N, $\delta^{13}C$, $\delta^{15}N$, measurement uncertainty, palaeoclimate