Widening the application of compound-specific isotope analysis to less volatile molecules

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Since the GC/C/IRMS was commercially available, compound-specific isotope analysis (CSIA) has been a routine tool for organic geochemistry [1]. However, most biochemical molecules such as proteins are less volatile (high polarity and high molecular weight), which are not amenable to GC/C/IRMS. To apply CSIA to a wider range of organic compounds, several analytical systems have been developed; LC/C/IRMS (including a moving-wire technique) [2,3] and elemental analyzer (EA)/IRMS [4,5]. We have chosen the latter system and have improved the sensitivity of EA/IRMS to determine the isotopic compositions of a tiny amount of compounds (down to ~80 ngN) [5]. An advantage of this technique is that we can simultaneously measure both carbon and nitrogen isotopic compositions, whereas a disadvantage is that the target compounds have to be purified before the isotopic measurement. Purification is generally achieved by either capillary PCGC or HPLC. The purification process is generally time-consuming, and thus, the technique does not fit for producing routine measurements of many samples. Whether such efforts are worth making depends on the necessity of the isotopic data. In this presentation, I will show our applications of this method to various molecules including chlorophylls, porphyrins, amino acids, and some enzymes, as well as the technical improvements of the EA/IRMS.

[1] Hayes *et al*. (1990) *Org Geochem* **16**, 1115-1128. [2] Caimi *et al*. (2008) *Anal Chem* **65**, 3497-3500. [3] Sessions *et al*. (2007) *Anal Chem* **77**, 6519-6527. [4] Polissar *et al*. (2007) *anal Chem* **81**, 755-763. [5] Ogawa *et al*. (2014) in *Earth, Life, and Isotopes*. pp.339-353.