

## Analytical optimization of achiral and chiral amino acids for compound-specific and enantiomer-specific isotope studies.

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Since the time of Pasteur, the development of biomolecular chirality has remained one of the most important problems with regard to our knowledge concerning chemical evolution. The homochiral amino acids and sugars are essential to the formation, structure, and function of biopolymers and are a defining molecular trait of life on the Earth [1] (cf. asymmetric photochemical processes [2]). Meteorites, specifically carbonaceous chondrites, carry pristine abiotic signatures of molecular chirality in the solar system. Enantiomeric excesses of L-form  $\alpha$ -methyl amino acids are found in the CM meteorite Murchison and the CI meteorite Orgueil with the correlation of hydro-alteration processes in the parent body [3]. For further information of compound-specific and enantiomer-specific nitrogen isotopic composition, here we developed the analytical optimization for achiral and chiral amino acids.

The precise determination of amino acids in calcareous, siliceous, geological samples (including mineral matrix in C-type meteorites) is troublesome, since extracts of these samples often contain a significant amount of interfering organic and inorganic substances. To overcome this critical issues, at first we employed cation-exchange chromatography of protein and non-protein amino acids prior to derivatization for gas chromatographic separation, including gas chromatograph/ combustion/ isotope ratio mass spectrometry (GC/C/IRMS) [4,5]. Among the wet chemical treatment, we confirmed that the average recovery of amino acids was better than 94% and there was no nitrogen isotopic fractionation [5]. Pre-treatment of an extract has two advantages: (i) Separation from complex hydrophilic compounds, including sugars and organic acids, which consume derivatization reagents during esterification, (ii) desalting of inorganic compounds derived from matrix minerals, thereby preventing damage to the combustion and reduction furnaces in the system. We occasionally use ion-pair liquid chromatography combined with electro-spray ionization mass spectrometry (LC/ESI-MS) for further compound isolation [unpublished].

A remarkable feature of the nitrogen isotopic compositions of bulk organics from various carbonaceous chondrites is that they are significantly higher than those of terrestrial materials, up to +3200‰ (vs. Air) [6]. We successfully applied the present optimized procedure to representative carbonaceous meteorites [7], including wide variety of geological samples. We believe that application of compound-specific nitrogen isotopic analysis will reveal the role of individual amino acids and open up our knowledge of the abiotic chemical processes [8].

**References:** [1] Meierhenrich, 2008. *Amino acids and the asymmetry of life*, Springer, pp. 1-241. [2] e.g., Takano et al., 2007. *Earth Planetary Science Letters*, 254, 106-114; Meinert et al., 2011. *Physics Life Reviews*, 8, 307-330. [3] Glavin and Dworkin, 2009. *PNAS*, 106, 5487-5492. [4] Chikaraishi et al. 2010. *Earth, Life, Isotopes*, Kyoto Univ Press., pp. 367-386. [5] Takano et al. 2010. *Rapid Communications Mass Spectrometry*, 24, 2317-2323. [6] Busemann et al. 2006. *Science*, 312, 727-730. [7] Chan et al., 2013. Abstract of Hayabusa Symposium in this issue. [8] Ohkouchi and Takano, 2013. Organic nitrogen: sources, fates, and chemistry. *Treatise on Geochemistry*, in press.