Goldschmidt 2022 Abstract
https://doi.org/10.46427/gold2022.12538

Position-specific carbon isotopes of Murchison amino acids elucidate extraterrestrial abiotic organic synthesis networks

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Murchison is a well-studied carbonaceous chondrite with high concentrations of amino acids ('AA's'; ~60ppm total), many of which have high $\delta^{13}C$ values suggesting they are dominantly endogenous to the meteorite. For instance, alanine (~16.5nmol per g) [1] has $\delta^{13}C_{VPDB}$ values of 38±10‰ (D) and 40±9‰ (L) [2]. Past studies have proposed extraterrestrial AA's in Murchison could have formed by Strecker synthesis (for α-AA's), Michael addition (for β-AA's), or reductive amination. Position-specific isotope analysis may discriminate among these mechanisms by relating molecular sites to isotopically distinct carbon sources, and by constraining isotope effects associated with elementary chemical reactions. A past study measured the position-specific carbon isotope composition of alanine and demonstrated that alanine's high $\delta^{13}C_{VPDB}$ value is attributable to the amine site ($\delta^{13}C_{VPDB}$ = 142±20‰), consistent with Strecker synthesis drawing on ^{13}C-rich carbonyl groups in precursors [3]. In contrast, aspartic acid and β-alanine are abundant on Murchison (2.65 and 16nmol per g, respectively) [1], but have lower molecular average $\delta^{13}C_{VPDB}$ values ($\delta^{13}C_{aspartic\ acid}$ = 4‰ (D+L; [4]); $\delta^{13}C_{b\text{-}alanine}$ = 4.9‰ [2]). Aspartic acid's dicarboxylic structure suggests it may have been formed via distinct synthesis processes from those of other α-AA's, while β-alanine could have been formed via Michael addition or via decarboxylation of aspartic acid [2]. Here, we measured the carbon isotopic composition of derivatized aspartic acid and β-alanine fragments via QExactive GC-Orbitrap, constraining position-specific $\delta^{13}C$ values relative to lab standards. We found aspartic acid's amine site has a $\delta^{13}C$ value of 8±5‰, demonstrating it was synthesized from distinct precursors from alanine – potentially HCN via dicarboxylic or α-keto acid intermediates with low $\delta^{13}C$ values. β-alanine's amine site has a $\delta^{13}C$ value of 60±24‰, which supports formation from ^{13}C-rich precursors via a Michael addition mechanism. Taken together, these measurements highlight the complexity of extraterrestrial organic synthesis networks, and show that emerging methods of isotope ratio analysis are capable of revealing the details of those networks.

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