

### Synthesis of $^{13}\text{C}$ -enriched amino acids with $^{13}\text{C}$ -depleted IOM in a formose-type reaction.

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**Introduction:**  $^{13}\text{C}$ -enrichment is one of the representative characteristics of meteorite's small organic compounds such as amino acids, nucleobases, and sugars [1-3]. The reason for this enrichment has not been clear but discussed as the contribution of  $^{13}\text{C}$ -enriched organic compounds formed in extremely cold outer protosolar disk or the molecular cloud [e.g., 1, 2]. Conversely, IOM, the major organic matter in carbonaceous chondrites, is depleted in  $^{13}\text{C}$  [4]. The different enrichments of  $^{13}\text{C}$  in the different organic compounds in the same meteorites may provide useful information on their origins.

Formose-type reaction is one of the proposed mechanisms on the origin of IOM, amino acids, and sugars found in meteorites [2,5,6]. We hypothesized that kinetic isotope fractionation in this type of reaction created different enrichment of  $^{13}\text{C}$  in different product organics and conducted the simulation experiments.

**Experimental:** Aqueous solution containing formaldehyde ( $\delta^{13}\text{C} = -42.6\text{‰}$ ), glycolaldehyde ( $\delta^{13}\text{C} = -16.7\text{‰}$ ), ammonia, and calcium hydroxide was heated at  $80^\circ\text{C}$  for up to 90 days. Yields of amino acids, amines, carboxylic acids, formaldehyde, and IOM were analyzed with LC-MS and GC-MS. The  $\delta^{13}\text{C}$  values of amino acids, IOM, and the bulk solution were analyzed with gas chromatography–combustion–isotope ratio mass spectrometry (GC-c-irMS) and elemental analyzer isotope ratio mass spectrometry (EA-irMS).

**Results and Discussion:** The product solution contained both soluble and insoluble organic matter. The insoluble organic matter was regarded as IOM analog. The IOM analog has close  $\delta^{13}\text{C}$  values to the bulk aldehydes in the starting material (i.e.,  $\delta^{13}\text{C} \sim -30\text{‰}$ ), whereas the product amino acids were enriched in  $^{13}\text{C}$  by up to 47.8‰ than the product IOM analog. This difference is consistent with the difference of  $\delta^{13}\text{C}$  values of  $\alpha$ -amino acids and IOM in primitive carbonaceous chondrites. This difference would have been provided by the kinetic isotope effects in this reaction. The reaction consumed formaldehyde rapidly with the latter formation of amino acids. This indicates that amino acids were formed using remaining formaldehyde that was enriched in  $^{13}\text{C}$  by kinetic isotope effects during the formaldehyde consumption before amino acid synthesis. Compositions of amines and carboxylic acids are similar to their compositions in the Murchison meteorite.

These results indicate that the formose-type reaction simultaneously forms  $^{13}\text{C}$ -enriched amino acids with  $^{13}\text{C}$ -depleted IOM. This type of reaction might have happened in asteroids and the proto-solar disk because both thermal and photochemical formose reaction is possible. Therefore,  $^{13}\text{C}$ -enriched organic compounds formed in the extremely cold solar system were not needed to explain the  $^{13}\text{C}$ -enriched small organic molecules in meteorites. Alternatively, thermal/photochemical formose-type reactions in the protosolar disk and in asteroids created the isotope enrichments in a wider area of the early solar system.

**References:** [1] S. Pizzarello, Y. Huang, M. Fuller (2004) *Geochim. Cosmochim. Acta* 68, 4963–4969. [2] J. E. Elsila, S. B. Charnley, A. S. Burton, D. P. Glavin, J. P. Dworkin (2012) *Meteorit. Planet. Sci.* 47, 1517–1536. [3] Y. Furukawa, Y. Chikaraishi, N. Ohkouchi, N. O. Ogawa, D. P. Glavin, J. P. Dworkin, C. Abe, T. Nakamura (2019) *Proc. Natl. Acad. Sci. U.S.A.* 116, 24440–24445. [4] C. M. O'D. Alexander, M. Fogel, H. Yabuta, G. D. Cody (2007) *Geochim. Cosmochim. Acta* 71, 4380–4403. [5] G. D. Cody, E. Heying, C. M. O. Alexander, L. R. Nittler, A. L. D. Kilcoyne, S. A. Sandford, R. M. Stroud (2011) *Proc. Natl. Acad. Sci. U.S.A.* 108, 19171–19176 (2011). [6] Y. Kebukawa, Q. H. S. Chan, S. Tachibana, K. Kobayashi, M. E. Zolensky (2017) *Sci. Adv.* 3, e1602093.