

The 10 new amino acids identified in the Murchison meteorite: A suggestion of new formation pathways of meteoritic amino acids

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Introduction: Carbonaceous chondrites contain a diverse suite of extraterrestrial amino acids [1]. The amino acid distribution (e.g. α -aminoisobutyric acid and β -alanine [2]) and L-enantiomeric excess (Lee) of isovaline [3] could be correlated with the degree of aqueous alteration. Although these results suggest that aqueous alteration has influence on amino acid synthesis on the meteorite parent body, the detailed formation mechanisms remain unclear. In this work, we revisited amino acid analysis of the Murchison meteorite to pursue their formation pathways and performed the amino acid synthesis experiments simulating the condition of meteorite parent body: the aqueous solution (300 μ L) containing ammonia/formaldehyde/acetaldehyde and/or glycolaldehyde (100/10/1/1 by mol) with $\text{NH}_3/\text{H}_2\text{O}$ (1/100) was heated at 60 °C for 6 days in a N_2 -purged glass ampoule with or without olivine powder (San Carlos, 27.0 mg).

Results and Discussion: Totally 29 amino acids between C_2 and C_6 were identified in the extract of Murchison, in which glycine was the most abundant (up to approximately 3.0 ppm). In addition to the amino acids reported previously, the nine C_3 and C_4 hydroxy amino acids (isoserine, homoserine, γ -amino- α -hydroxybutyric acid, γ -amino- α -(hydroxymethyl)propionic acid, β -homoserine, β -amino- α -hydroxybutyric acid, α -methylserine, isothreonine and allo-isothreonine, ranged from ~20 to ~140 ppb) have been newly identified from the Murchison extract. A new dicarboxy amino acid, β -(aminomethyl)succinic acid, was also detected as a relatively large peak (~90 ppb). The discovery of 10 new amino acids is striking after numerous surveys of meteoritic amino acids since the half century ago.

The simulation experiments gave various amino acids including the hydroxy amino acids with the most abundant of glycine as identified in the Murchison extract. The hydroxy amino acids were identified using glycolaldehyde in addition to formaldehyde, acetaldehyde and ammonia. Moreover, β -(aminomethyl)succinic acid was produced using formaldehyde, acetaldehyde and ammonia in the presence of olivine, but not detected in the absence of olivine. These results indicate that formose reaction with ammonia in the presence of minerals is an important formation pathway to produce meteoritic amino acids during aqueous alteration on the meteorite parent body.

References: [1] Burton A. S. et al. (2012) *Chem. Soc. Rev.*, 41, 5459-5472. [2] Glavin D.P. et al. (2006) *Meteor. Planet. Sci.*, 41, 889-902. [3] Glavin D. P. and Dworkin J. P. (2009) *Proc. Natl. Acad. Sci. USA*, 106, 5487-5492.

Origin and evolution of water and organic compounds in the CM carbonaceous chondrites.

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Introduction: Organic matter (OM) and hydrated minerals found in chondrites are the remnants of primordial reservoirs present in the protoplanetary disk 4.6 billion years ago. Nevertheless, it is unclear how their primordial chemical and isotopic signatures might have been modified by chemical reactions occurring on asteroidal parent bodies [e.g. 1]. The CM-type carbonaceous chondrites constitute a well-identified chemical group of chondrites that presents a wide range of hydrothermal alteration degrees on their parent body and may be one of the dominant sources of meteoritic material fallen on Earth [2]. CM chondrites are thus valuable samples to study the origin and evolution of the primordial signatures of OM and water in the Solar System.

In this study, we analysed the D/H and C/H ratios in the fine-grained matrices of different CM chondrites at the scale of some micrometers to trace the interactions between OM and water on the CM- carbonaceous chondrite parent body.

Experimental: Sub-millimeter pieces of 6 CM chondrites (from the most altered to the least altered: Sayama, Cold-Bokkeveld, Murray, Mighei, Murchison, Paris) were pressed in indium foils. Fine-grained matrix areas were selected under optical and electron microscopes. The SIMS IMS1280-HR at Hokkaido University was used to measure their D/H and C/H ratios on areas of 10 x 10 μm^2 with a Cs^+ primary beam.

Results and discussion: Depending on the position of the primary beam on the matrix, the D/H and C/H ratios vary as a function of the relative amount of OM to hydrated minerals. Positive correlations between these ratios are found in all the CM matrices. For all CMs but Paris, the positive correlations indicate that their H isotopic compositions can be explained by a mixing between a D-rich OM and a D-poor water having an isotopic composition of $\delta\text{D} = -350$ ‰. For Paris, the least altered lithologies show a clear D-enrichment comparing to other CMs, while the more altered lithologies tend to have a H isotopic distribution closer to the other CMs. These results indicate that no significant isotope exchange occurred between OM and water, as it should have enhanced the D/H ratio of water in the more altered meteorites. The D-rich points of Paris could be explained by the presence of a third mixing component, a D-rich water, that could originate from low temperature regions. The presence of two sources of water in the Paris chondrite is consistent with recent carbonate oxygen isotope measurements [3].

References: [1] Alexander et al. (2012) *Science* 337, 721-3. [2] Gounelle et al. (2005) *GCA* 69, 3431-3443. [3] Vacher et al. (2016) *ApJ* 827:L1.