

Molecular descriptors for dictating the aqueous-alteration-induced organic decomposition in carbonaceous chondrites and return sample from Ryugu asteroid

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Background. Carbonaceous chondrites (CCs) are among the most primitive material in our Solar System. Organics such as amino acids are ubiquitously found in CCs and have been invoked to serve as life's building blocks to promote the origin of life on Earth and possibly elsewhere. Meanwhile, the chemical diversity of amino acids records the chemical evolution events prior to and after the accretion of their parent bodies. In the past decade, the advancement of analytical instrumentations, an increasing supply of samples from various CC subgroups, and the development of a more accurate petrographic classification system of CCs have facilitated the study on how parent body processes have shaped the organic distributions. However, there is a large discrepancy between experimental results and meteoritic records. Previous studies show that amino acids can be synthesized in aqueous solution containing primordial molecules, suggesting that amino acids would have accumulated upon extended aqueous activity. Nevertheless, amino acids are found to be depleted in more aqueously altered CCs, pointing to a potential "Water Paradox".

In our previous study [1], we discovered a new low-temperature geo-electrochemical process which provides a possible solution to the "Water Paradox" and proposed a new molecular descriptor of aqueous alteration degree. The geo-electrochemistry model was proposed based on the redox gradient that could be generated via water/rock interaction (Fig. 1). H₂ gas, generated through water/rock interaction, serves as the electron donor to drive the geo-electrochemical alteration of amino acids at the interface of mantle fluid and minerals. We found that three model amino acids (glycine, alanine, and valine) were decomposed to their amine and hydroxy acid analogs, and both of these two compound classes were found to coexist with amino acids and enriched in heavily aqueously altered CR chondrites. These results suggest that decomposition of amino acid dominates the chemical evolution of the parent body of CR chondrites. However, the discussion was only limited to CR chondrites due to insufficient data of amine and hydroxy acid abundances in other CC subgroups.

Recently, we extended this model to other types of amino acids and found that the electrolysis of glutamate (Glu) and aspartate (Asp) generates γ -aminobutyrate (γ -ABA) and β -alanine (β -Ala), respectively, via reductive decarboxylation. The enrichment of these products with respect to their amino acid precursors is found in heavily aqueously altered CR 2.0–2.4, CI as well as a return sample from asteroid Ryugu. These data suggest that the relative enrichment of derivative products can serve as a general descriptor of aqueous-alteration-induced organic decomposition. A geochemical model based on the water-rock differentiation in the parent icy planetesimals [2] was proposed to account for the observation.

Experiments and results. Electrolysis of amino acids was conducted at ambient temperature (25 °C) in an electrochemical cell made of two compartments separated by a proton-exchange membrane. In the cathodic chamber, iron or nickel sulfide catalysts were placed on a carbon paper electrode in a pH-7 phosphate buffer containing 20 mM of Glu or Asp. An anoxic condition was maintained by continuous argon gas flow during electrolysis. Using these two sulfides as catalysts, the conversion of Glu and Asp to various products, including decarboxylated products (γ -ABA and β -Ala, respectively), α -hydroxy acids (2-hydroxyglutarate and malate, respectively) was observed after 14-day electrolysis of amino acids at $-0.5\sim-1.0$ V versus standard hydrogen electrode (vs. SHE). The electrode potential represented the magnitude of the redox gradient (H₂ enriched core versus bicarbonate-buffered mantle) and is equivalent to the reduction potential of H₂/H⁺ redox

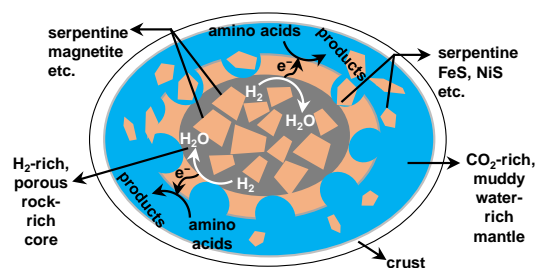


Figure 1. Model of geo-electrochemical alteration of amino acids induced by water-rock interaction in icy planetesimals (a parent body of CCs). A difference in the water/rock mass ratio (W/R) between the core (grey) and mantle (blue) leads to gradients in pH and redox.

couple under specific pH and temperature conditions. A more negative electrode potential corresponds to a condition with more alkaline pH or higher temperature.

Discussion. The well-documented abundances of these four chemically related amino acids (namely, Glu, Asp, γ -ABA, and β -Ala) among different CC subgroups allow a general comparison of amino acid distribution and discussion on the impact of aqueous-alteration-induced decomposition processes (Fig. 2). Although no clear tendency can be deduced from the absolute abundances of these amino acids (Fig. 2a-2d) among different CCs, obvious enrichments of γ -ABA over Glu (Fig. 2f) and β -Ala over Asp (Fig. 2e) were discovered among heavily aqueously altered CR2.0–2.4, CI chondrites; contrastively, such enrichments are not observed in CM1–2.9 and primitive CR2.7–2.8 chondrites. Such difference implies that the impact of geo-electrochemical decomposition of amino acid highly depends on the chemical composition, degree of water-rock differentiation and the location of parent bodies in the early Solar System (Fig. 2i-2j). While we do not rule out parent body formation at various locations to account for different degree of aqueous-alteration-induced organic decomposition, here we propose another scenario where CI, CM and CR sample different regions of water-rock-differentiated parent icy planetesimals formed beyond the CO₂ snow line. The accreted CO₂ ice and H₂O ice were melted by the heat generated via the decay of short-lived radionuclides. The icy planetesimal experienced water-rock differentiation and features a rock-rich core and water-rich mantle as discussed by Kurokawa et al. [2]. The low water/rock mass ratio (W/R) in the core generated alkaline, H₂-rich fluid upon water/rock interaction. In contrast, the high W/R ratio in the mantle generated neutral to weakly alkaline, CO₂-rich fluid where geo-electrochemistry proceeded and decomposed Glu and Asp to γ -ABA and β -Ala, respectively. Therefore, in light of the high abundance ratio of γ -ABA/Glu and β -Ala/Asp in CI and CR 2.0–2.4 chondrites, it is possible that these chondrites originally sourced from the mantle (Fig. 2i-2j). This is consistent with the observation of similarly high enrichment in the samples obtained from the surface of Ryugu asteroid (Fig. 2e~2h), which was suggested to be CI-like body with an outer Solar System origin [5, 6] and processed by low temperature aqueous alteration (30 °C) [6]. In contrast, the very low abundance ratios revealed in CM1–2 and CR2.7–2.8 chondrites indicate that they were sourced from the rock-rich core, as no geo-electrochemical alteration of amino acid could proceed there. CR should span a wide range of rock/mantle transition region, thus show a wide range of decomposition degree. Based on these results and discussions, we propose that the relative abundance ratios of derivative products/organic precursors can serve as a general molecular descriptor for dictating the aqueous-alteration-induced organic decomposition as well as shedding insight into the water/rock differentiation status of icy planetesimals at their early evolution period [2]. This can shed implications on the chemical evolution and cycling within the parent bodies, as well as provide chemical models for guiding the future space missions to asteroids and return sample analyses.

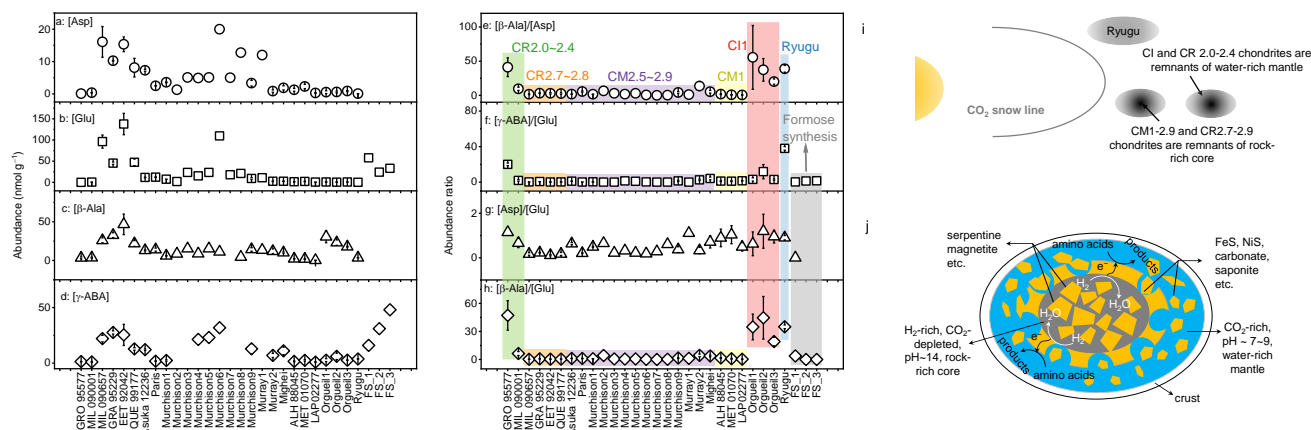


Figure 2. The molar abundances of aspartate (a), glutamate (b), and the decarboxylated products β -Ala (c), and γ -ABA (d) in different carbonaceous chondrites and Ryugu sample reported recently [3]. FS_1–3 indicates the Formose-type synthesis results at 90–150 °C reported by Kebukawa et al. [4]. e, f, g, and h plotted the molar ratios of β -Ala/aspartate, γ -ABA/glutamate, aspartate/glutamate, and β -Ala/glutamate, respectively, in these samples. i and j depicted the model that can explain the different decomposition degree in e–h among different carbonaceous chondrite subgroups resulted from geo-electrochemistry in a water-rock differentiated parent body.

References

- [1] Y. Li et al. *Nat. Commun.* **2022**, 13:4893. [2] H. Kurokawa et al., *AGU Adv.* **2022**, 3(1). [3] E. T. Parker et al., 53rd Lunar and Planetary Science Conference, **2022**, 2651. [4] Y. Kebukawa et al., *Sci. Adv.* **2017**, 3 : e1602093. [5] T. Yada et al., *Nat. Astron.* **2022**, 6(2). [6] M. Ito et al., *Nat. Astron.* **2022**.