

EFFECTS OF MINERAL ASSEMBLAGES IN METEORITES ON AMINO ACID PRODUCTION IN THE WATER-BEARING PARENT BODIES.

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Introduction: Carbonaceous chondrites are the most primitive known meteorites; therefore, they are considered as extraterrestrial samples of the solar system that maintain records of prebiotic chemistry and can offer clues about the conditions present during the early solar system. Carbonaceous chondrites contain a wide variety of organic compounds, including amino acids, indicating prebiotic organic chemistry before and during the formation of the solar system. It was recently proposed that formaldehyde reactions produced part of the meteoritic organic matter [1]. Kebukawa et al. [2,3] demonstrated that the inclusion of ammonia enhances the yields of organic matter from formaldehyde and simultaneously produces amino acids.

Some carbonaceous chondrites are aqueously altered, while others are thermally metamorphosed; CI, CM, and CR chondrites are aqueously altered chondrites, while CV, CO, and ordinary chondrites have experienced low degrees of aqueous alteration and moderate thermal metamorphism. Carbonaceous chondrites are a primordial subclass of stony meteorites comprised primarily of silicates, which could play a significant role in the evolution of meteoritic organic matter during hydrothermal processes. The presence and nature of silicates could affect the molecular distribution of the organic compounds including amino acids in these primitive bodies [4–6]. CM and CR are characterized by abundant phyllosilicates, while olivine and pyroxene are the main minerals in CV [7,8]. Olivine and phyllosilicates have been proposed as catalysts for the synthesis of organic molecules in the early Solar System [9,10]. Previously, we have investigated the effects of minerals; olivine, montmorillonite, and serpentine for amino acid production from formaldehyde and ammonia in conditions simulating water-bearing meteorite parent bodies [6]. In the current research, we evaluated the effects of meteorite powders for amino acid production under the same experimental conditions, to evaluate the direct effects of mineral assemblages of carbonaceous chondrites

Method: Aqueous alteration in meteorite parent bodies were simulated by using an aqueous mixture of formaldehyde and ammonia in the presence of water, at a molar ratio of $\text{H}_2\text{CO}:\text{NH}_3:\text{H}_2\text{O} = 9:1:100$ (5 M H_2CO and 0.6 M NH_3) at 150 °C under different heating duration (1 d, 3 d, or 7 d). We refer to the product as “FAW” after formaldehyde–ammonia–water. Meteorite powders were added (2 mg per 200 μL of solution) to

the FAW solution mixture to examine their catalyzing/inhibiting impact on amino acids formations. Control samples were prepared using a starting solution containing formaldehyde and water (without ammonia) at a molar ratio of $\text{H}_2\text{CO}:\text{H}_2\text{O} = 9:100$. The used meteorites were Murchison (CM2), Miller Range (MIL) 090001 (CR2), and Allende (CV3). The soluble compounds were previously extracted from these meteorite powders with dichloromethane (DCM) for other purposes. To extract indigenous amino acids before the heating experiments, an aliquot of each powdered meteorite was flame-sealed in test tubes with 1–2 mL ultrapure water per 0.5–1 g of powder and incubated in a heating block at 110 °C for 24 h, following the typical hot-water extraction technique. After the heating experiments, the FAW with meteorites were acid hydrolyzed using 6 M HCl at 110 °C for 24 h, dried, underwent desalting with a cation-exchange resin (AG 50W-X8 resin). The resulted products were analyzed using high-performance liquid chromatography (HPLC).

Results: Amino acid concentrations. The aqueous solution of formaldehyde and ammonia produced various kinds of amino acids after acid hydrolysis. For FAW without minerals, the total amino acid concentration increased after heating for 7 d [6]. However, these results changed in response to the addition of meteorites, and the concentrations of the amino acids had responded differently according to different meteorites (Figure 1a). In presence of Murchison, the total amino acids concentrations were increased after increasing the heating duration from 1 d to 3 d, then the total amino acid yields were almost constant from 3 d to 7d. MIL 090001 had a different effect on amino acid production, since the production of

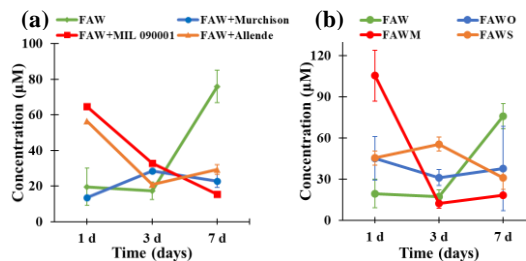


Figure 1. Total amino acid concentrations of Asp, Glu, Ser, Gly, β -Ala, and Ala of the FAW heated at 150 °C for 1 d, 3 d, and 7 d after acid hydrolysis. Note: without minerals “FAW”, with olivine “FAWO”, with montmorillonite “FAWM”, and with serpentine “FAWS”.

the amino acids at 1 d was the highest among all tested samples, whereas the amino acid concentrations decreased constantly after heating for 7 d to the lowest observed concentration. Allende enhanced amino acid production at 1 d, decreased at 3 d, increased again after 7 d. Meteorites showed catalytic effects for the production of the amino acids after heating at 150 °C at 1 d and 3 d. After 7 d, all meteorites enhanced amino acid decomposition. Consequently, we suggest that meteorites behave similarly to our previous experiments using silicates (Figure 1b) [6], as they enhanced the amino acid production at a shorter heating duration, but they turned out to enhance their decomposition during longer heating periods. In FAW with Murchison, Gly is the predominant at 1 d, and most amino acids increased from 1 d to 3 d, then became relatively stable until 7 d. In FAW with MIL 090001; Gly and β -Ala are dominants at 1 d, and most amino acids are stable from 1 d to 3 d, then decreased until 7 d. In FAW with Allende: Gly, β -Ala, and Leu are dominants at 1 d, and most amino acids decreased from 1 d to 3 d then become stable, however, some of them increased from 3 d to 7 d (Figure 2).

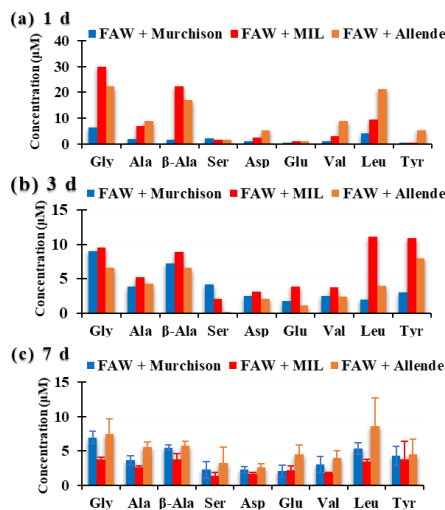


Figure 2. Amino acid concentrations of the FAW heated at 150 °C for 1 d, 3 d, and 7 d after acid hydrolysis.

Discussion: Studies have revealed that α -amino acids are abundant in the Murchison CM2 chondrite [11,12], as well as through hydrothermal synthesis experiments [13,14]. In contrast, in the aqueously altered CR chondrites such as MIL 090001, which was subjected to extended aqueous alteration compared to Murchison, β -Ala was predominant [11,12]. Although the aqueous alteration process was rather lower temperatures and longer durations compared to the laboratory experiments, these are consistent with our 7 d results since Gly was dominant in Murchison, while in MIL 090001, Gly and β -Ala have equal quantities and became predominates.

The dominant minerals in CV chondrites are olivine and pyroxene [7], while phyllosilicates are abundant in CM and CR chondrites. Therefore, by comparing our meteorite results with our prior mineral results (Figure 3) [6], we found that Gly, Ala, and β -Ala concentrations are almost the same at 3 d and 7 d in both FAW with olivine and Allende. Gly, Ala and, β -Ala concentrations are almost the same at 7 d in results of FAW with serpentine, montmorillonite, Murchison, and MIL090001.

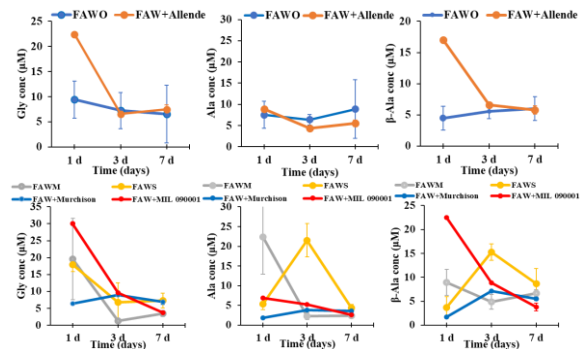


Figure 3. Gly, Ala, and β -Ala concentrations of the FAW with minerals and meteorites heated at 150 °C for 1 d, 3 d, and 7 d after acid hydrolysis.

Conclusion: Our results implied that meteorites showed both positive and negative effects on amino acids production in aqueous environments and that the amino acids could have different response behaviors according to the kind of dominant minerals in each meteorite, although our experimental conditions were limited. We suggested that the concentrations of the amino acids depend on 1) the kind of dominant minerals in each meteorite, 2) the stability of the amino acid during the longer heating durations, and 3) the degree of aqueous alteration on the parent bodies of carbonaceous chondrites.

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