

ABIOTIC SYNTHESIS OF ORGANIC MATTER IN AQUEOUS ENVIRONMENTS SIMULATING PARENT BODIES OF METEORITES AND THE EFFECTS OF MINERALS ON THE PRODUCTION OF AMINO ACIDS. Walaa Elmasry¹, Yoko Kebukawa¹, Takazo Shibuya², and Kensei Kobayashi¹, ¹Graduate School of Engineering Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, ² Super-cutting-edge Grand and Advanced Research (Sugar) Program, Institute for Extra-cutting-edge Science and Technology Avant-garde Research (X-star), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan. (Email: walaa-elmasry-hm@ynu.jp).

Introduction: Carbonaceous chondrites contain a wide variety of organic compounds, including amino acids, which provide records of the prebiotic organic chemistry before and during the solar system formation. Recently, it was suggested that some of the meteoritic organic matter was produced through reactions of formaldehyde [1]. Furthermore, Kebukawa et al. [2,3] showed that the presence of ammonia enhances the yields of organic matter from formaldehyde, and simultaneously producing amino acids.

During the hydrothermal processes, minerals in parent bodies could play an important role in the evolution of meteoritic organic matter. It was suggested that olivine and phyllosilicates could act as catalysts for the reactions of organic precursor molecules in the early Solar System [4,5]. The different chemical composition of the phyllosilicates, possibly leading to different catalyzing/inhibiting organic reactions including amino acid formation [6,7]. In the current research, we evaluated the effects of minerals for amino acid production from formaldehyde and ammonia in the conditions simulating water-bearing meteorite parent bodies.

Method: Aqueous alteration in meteorite parent bodies were simulated by using an aqueous mixture of formaldehyde and ammonia with 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. Moreover, minerals which are typical in meteorites, were added (10 g/L) to the FAW solution mixture to examine their catalyzing/inhibiting impact on amino acids formations. The used minerals were olivine ($(\text{Mg}, \text{Fe})_2\text{SiO}_4$) from San Carlos, Arizona, USA, Na-montmorillonite ($(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg}, \text{Fe})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$) — “SWy-1” from the Clay Minerals Society, and serpentine (antigorite) ($(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$) from Miyatsu, Kyoto, Japan. The resulted products were analyzed using high performance liquid chromatography (HPLC) after acid hydrolysis and dried soluble fractions were analyzed using Fourier transform infrared (FTIR) microspectroscopy (see details for [8]). Moreover, a laboratory-based simulation experiments using Geochemist's Workbench 14.0 (GWB 14.0) software

were conducted.

Results and Discussion: *Amino acid concentrations.* The aqueous solution of formaldehyde and ammonia produced various kinds of amino acids after acid hydrolysis [8]. In the FAW without minerals, at 1 d, Gly was the dominant amino acid, yet after 3 d and 7 d, Ala and β -Ala showed a significant increase and became dominants (Figure 1). It could be explained primarily by the amino acid decomposition process during thermal alteration of the organic matter via α -decarboxylation, e.g., the decomposition of Asp leading to the formation of β -Ala [9]. Many studies have revealed that α -amino acids are abundant in the Murchison CM2 chondrite [9,10], as well as through hydrothermal synthesis experiments [11,12]. In contrast, in the CI1 chondrites Orgueil and Ivuna, which were subjected to an extended aqueous alteration compared to CM2 chondrites, β -Ala is the most abundant [9,10]. This is consistent with the relative decrease of Asp with time in our experiments and increase of β -Ala.

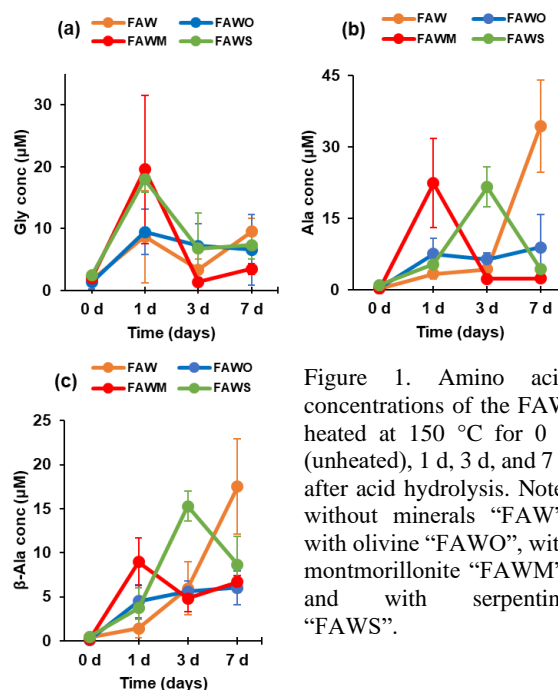


Figure 1. Amino acid concentrations of the FAW heated at 150 °C for 0 d (unheated), 1 d, 3 d, and 7 d after acid hydrolysis. Note: without minerals “FAW”, with olivine “FAWO”, with montmorillonite “FAWM”, and with serpentine “FAWS”.

Minerals showed catalytic effects for the formation of amino acids at shorter heating duration (1 d), especially with montmorillonite (Figure 2), probably

due to its high surface areas and small pore sizes [13]. Olivine and serpentine enhanced amino acids production for 1 d and 3 d. After 7 d, all minerals enhanced amino acid decomposition. Consequently, we suggested that minerals enhanced the amino acid production at shorter heating duration, but they turned out to enhance their decomposition for longer heating.

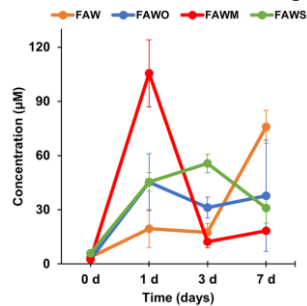


Figure 2. Total amino acid concentrations which include Asp, Glu, Ser, Gly, β -Ala, and Ala of the FAW heated at 150 °C for 0 d (unheated), 1 d, 3 d, and 7 d after acid hydrolysis.

FTIR absorption spectra. IR spectra revealed that the ester C=O/C=C peak intensity ratios in the presence of minerals (Figure 3) showed a lower value at short heating duration, maybe due to the enhancement of decarboxylation by minerals, and increased after heating for 7 d, which might be due to catalytic esterification by minerals. The presence of both Brønsted and Lewis acid sites in phyllosilicates can make them natural esterification catalysts [14]. Olivine also contains Lewis acid sites [15], which promote the esterification of FAW.

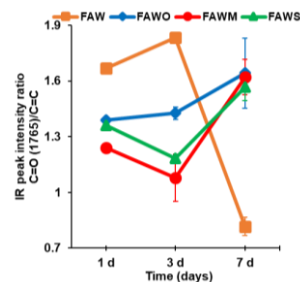


Figure 3. Trends in relative organic functional group concentrations with time for the soluble organics of FAW as determined by FTIR for the peak intensity ratios of C=O (ester)/C=C.

Thermodynamic calculation. Various amino acids have formed from FAW aqueous solution with the predominance of Gly and Ala. All amino acids increased to ~150 °C, whereas decreased with increasing the temperature (Figure 4). The calculated concentrations of amino acids were lower than those obtained through laboratory experiments. It probably due to the hydrolysis step in the laboratory analysis that liberates large amounts of amino acids, while the calculation treated the formation of free amino acids only, not amino acid precursors. The numerical calculation showed roughly the same behavior for our experimental analysis, as the FAW without minerals enhanced the Gly production with time (Figure 5), while phyllosilicates enhanced its decomposition after 7 d. Olivine demonstrated some stability in Gly concentration over

time. Further simulation experiments are needed to conduct in order to examine the effect of different chemical parameters, e.g., temperature and pH, on the stability of the amino acids as well as the alteration of minerals.

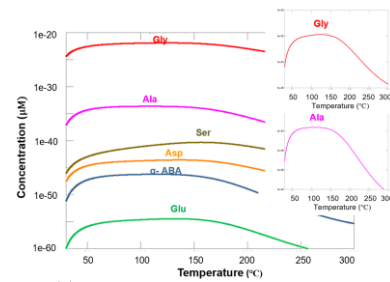


Figure 4. Concentration of amino acids (calculated by GWB) in the FAW system without minerals over thermal cycling (RT to 300 °C).

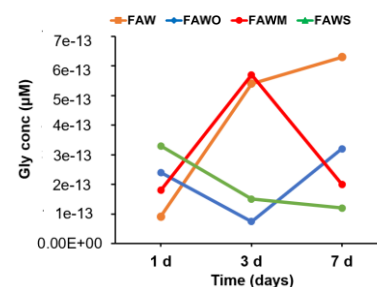


Figure 5. Glycine concentration (calculated by GWB) in the FAW system at 150 °C for 1 d, 3 d, and 7 d. (It should be noted that these results were calculated

based on the laboratory analysis of gaseous species, anions, and cations in the FAW samples).

Conclusion: Our results implied that minerals showed both positive and negative effects on the formation of amino acids in aqueous environments in small Solar System bodies and that the amino acids could have different response behaviors according to different minerals, although our experimental conditions were limited. We suggested that the concentrations of the amino acids depend on 1) the presence and the kind of minerals and 2) the stability of the amino acid during the longer heating duration.

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