

# *Evidence of the Existence of Proteinogenic Amino Acids in Space*

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**Abstract:** Proteinogenic amino acids – the primary monomers to form proteins on Earth – have been found successively in extraterrestrial areas over decades. It was reported that the detection of amino acids can be both ex situ and in situ. The discovery of proteinogenic amino acids from space may date back to the history of the solar system and is suggestive of alternative mechanisms of synthesizing amino acids. This article uses the literature review method and systematically summarizes the findings from meteorites, asteroids, comets, and the interstellar medium. The article concludes that complex organic molecules are widely spread across the universe and supports the hypothesis that the basic building block of life may be delivered to Earth via celestial bodies, increasing the likelihood of searching for living organisms outside Earth.

**Keywords:** the Murchison meteorite, asteroid Ryugu, comet 67P/Churyumov-Gerasimenko, interstellar medium

## 1. Introduction

The first time a proteinogenic amino acid was discovered traced back to 1970. Over 90 amino acids of different structures were identified in the Murchison meteorite, such as glycine, the simplest structured proteinogenic amino acid, and were confirmed not to be from terrestrial contamination. The field of analyzing and doing research for extraterrestrial amino acids began to emerge. By the early 21st century, scientific technologies and skills have been developed to maturity to allow in situ analysis of the composition of comets. In terms of lab work, methods including gas chromatography (GC) and mass spectrometry (MS) were applied to determine the configuration and abundance of amino acids. Instruments with high sensitivity and selectivity must be used to reduce co-elution. Scientists have extended the analysis dimension from 1D to 3D, also using instruments with higher resolutions.

The main sources of extraterrestrial amino acids are meteorites, asteroids, and comets. This article reviews one example from each source, and makes an argument about the detectability of amino acids in the interstellar medium (ISM), using glycine as an example. Glycine, interestingly, is the only amino acid which could be synthesized without liquid water.

This research field traces the origin of life through extraterrestrial biology and chemistry, recognizes the gap between our current knowledge and what remains unknown, and thus promotes the advancement of modern analytical techniques.

## 2. The Murchison meteorite

In September 1969, the Murchison meteorite fell in Australia. The fragments that broke apart from the parent object were used for analysis and the meteorite was classified as a carbonaceous chondrite of CM type, known for being rich in organic materials [1]. Samples with the fewest cracks and the least exterior contamination were chosen to analyze their composition [2]. After extraction and purification, the presence of amino acids (eg., Ala, Glu, Val, Pro) in L- and D- configurations were determined from GC and MS, with glycine having the highest concentration of 6 µg/g [3]. The presence of the amino acids was not due to terrestrial contamination for the following reasons: First, the interior sections of the meteorite were used in the experiment. Second, the amino acid which can be commonly found in human finger prints, serine, was only identified using the ion exchange chromatography (IEC), meaning that it had very low abundance in the meteorite sample [4]. And third, early studies showed that the L- and D-enantiomers were in racemic mixture, while all amino acids on Earth exhibit L-configuration [3,4].

However, later researchers overturned the previous conclusion that the amino acids from the Murchison meteorite existed in racemic mixtures. The L-enantiomer was in excess by 2.8% - 9.2% for some particular amino acids (eg., Glu, Asp, Pro, Leu, Ala) [5]. The observed disagreement could be attributed to progress in methodological frameworks [1]. Meteorites are susceptible when they bombard with the terrestrial ground. In one research of the Allende meteorite, another example of a carbonaceous chondrite of the same terrestrial age, contaminants were reached to a depth of 8mm, and may keep growing inward as time progresses [2]. By comparison with Murchison's physical features, such as surface fissures, grain size and porosity, at least 8mm from the surface of the meteorite should be removed before analysis. In the previous lab work, only 0.2mm thickness was removed, hence, the "interior" piece used for analysis was highly contaminated. Furthermore, the low abundance of serine and the absence of threonine cannot indicate that there was no contamination introduced, as these amino acids are likely to denature during the measurement of GC-MS. The absence of amino acids methionine, tyrosine and phenylalanine may be attributed to microbial contamination. Under the condition of hot water extract, which was a necessary step for the extraction of the meteorite, amino acids from the amino acid pool of microbes were released instead of the amino acids from the meteorite itself. The amino acid pool lacks methionine, tyrosine and phenylalanine and is therefore not present in the extract of the meteorite sample [2]. Moreover, the previous extraction method was thought to be flawed because of the acidic reagents, excessive reaction times and high temperatures [1]. Initially, the GC spectra showed co-elution between some amino acids. This problem was resolved by adopting the combined GC-MS method, which subsequently enabled the separation of amino acid peaks in later research. Finally, the hypothesis that chemical reactions might have occurred during the time interval between the bombardment and the experimental analysis of the meteorite is not impossible. Aqueous alteration probably could have occurred that changed the abundance of amino acids by preferential synthesis and decomposition of certain configurations of certain amino acids. Therefore, the current distributions of amino acids might not be exactly the same as the original distribution. The reasons behind the optical activities of amino acids on the Murchison meteorite remain an open question [6].

## 3. Asteroid Ryugu

The surface material from a Cb-type carbonaceous asteroid was brought back by the Hayabusa2 mission [7]. It was concluded that the parent asteroid of Ryugu formed 1.8-2.9 million years after the formation of the Solar system. Unlike the Murchison meteorite, the return of an extraterrestrial pristine sample minimized the likelihood of terrestrial contamination. The concentrations of total amino acids present were extremely diluted. In one study, a total of 18 different amino acids were

identified, with 13 of them being quantitated. The asteroid was analyzed by liquid chromatography (LC) with fluorescence detection and high-resolution mass spectrometry (HRMS); the amino acid concentration was reported to be less than  $30 \text{ nmol g}^{-1}$  [8]. The identification of a range of different amino acids, both proteinogenic and non-proteinogenic, revealed multiple possible distinctive routes of formation that could have been taken to synthesize these amino acids.

One-dimensional chromatographic separation was sometimes insufficient due to co-elution. Thus, a highly sensitive and selective three-dimensional high-performance liquid chromatography (HILIC) column combined with MS is preferred. The analytical system was tested using some other carbonaceous bodies prior to Ryugu. The amino acids were derivatized using 4-fluoro-7-nitro-2,1,3-benzoxadiazole fluorescence reagent, and then separated using reversed-phase, anion-exchange, and enantioselective columns [9]. The stereochemistry of more amino acids was revealed. Plausible mechanisms of amino acid formation were suggested to involve galactic cosmic radiation and ultraviolet photon mechanisms [8].

It is also intriguing to point out that after carrying out analysis with a three-dimensional high performance liquid chromatography with a high-sensitivity fluorescence detector (3D-HPLC/FD) and an ultrahigh performance liquid chromatography with fluorescence detection and high-resolution mass spectrometry (LC-FD/HRMS), the research group found out that the abundance of glycine appeared to be exceptionally lower by the measurement of LC-FD/HRMS than 3D-HPLC/FD. This was proven to be a result of evaporation; the loss rate of volatile species hydrogen cyanide and formaldehyde was accelerated. These two species could react with ammonia in alkaline conditions to form glycine, a process which is also known as Strecker synthesis. It was probable that Strecker synthesis had occurred during the aqueous alteration to produce  $\alpha$ -amino acids such as glycine. However, the existence of  $\beta$ -,  $\delta$ -, and  $\gamma$ - amino acids implied that there would be other hidden mechanisms. Those types of amino acids are more resistant to high temperatures. Therefore Ryugu was more likely to have experienced thermal or hydrothermal alteration more than aqueous alteration by the relative high abundance of straight-chain  $n$ - $\omega$ -amino acids and  $\beta$ -,  $\delta$ -,  $\gamma$ - typed amino acids in contrast with the low abundance of  $\alpha$ -amino acids (eg., glycine), which are less resistant to high temperatures [10]. The reflectance spectra (eg., Visible, near-infrared, and mid-infrared) did not show much variation across the surface of Ryugu, highlighting the low compositional diversity.

#### 4. Comet 67P/Churyumov-Gerasimenko

Rosetta marked the first spacecraft to orbit and land on a comet in 2014, this was the first time that an in-situ analysis was made [8]. As opposed to all other organic objects, in this particular case, no chemical sample preparation is involved. Besides, the absence of terrestrial contamination significantly enhanced the validity of the test results. Specifically, any glycine detected in the samples was conclusively attributed to non-terrestrial sources, as documented in reference [9]. Volatile glycine, together with precursor molecules methylamine and ethylamine, was discovered in the coma at a distance of 14 - 26 kilometers from the nucleus and was measured by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) mass spectrometer multiple times [11]. No information about the distribution of different conformations of glycine was provided [9].

A group of researchers hypothesized that glycine could possibly be emitted in three ways: directly ejected from the comet nucleus, then photolyzed; sublimation of solid glycine embedded on dust particles with 90% porosity that were ejected from the nucleus; sublimation of solid glycine embedded on water ice from dust particles that were ejected from the nucleus. After analysis, it was concluded that the first assumption was found to be inconsistent with the observation, and the second assumption could not explain the pattern and required an impractically large amount of glycine. The third assumption was proved to be the best fit with the observation. The glycine density profile was

calculated based on Haser's model assumptions, suggesting that the abundance of glycine in comet 67P was about 170 ppb [8].

## 5. Interstellar medium

Despite that amino acid precursors (aldehydes, ketones, ammonia, and hydrogen cyanide) have been found in the ISM region and three potential formation mechanisms of the amino acid glycine were determined, the existence of amino acids in ISM nonetheless remains skeptical as the obtained spectral lines did not prove the existence of glycine [12-14]. Studies have shown that the most stable form of the amino acid glycine of all isomers is its protonated form under gaseous conditions, yet glycine itself sublimates under 150°C [14]. The low abundance creates a challenge in detecting glycine and other amino acids. Until today, it still cannot be determined if there are any amino acids present in ISM with 100% certainty.

## 6. Conclusion

The discovery of amino acids on meteorites, asteroids, and comets suggests that celestial bodies might have played an important role in the arising of terrestrial life, acting as carriers to deliver prebiotic molecules to Earth. The emergence of analytical techniques allows more amino acids to be evaluated. The formation mechanisms of amino acids remain under investigation, along with the reason for the absence of stereochemical signatures in the biosphere.

The limitation of this article is its exclusive reliance on previously published work, with no experimental data obtained. Future research could be strengthened through additional lab investigations or simulations. Ideally, the procedure should be constructed and repeated in situ using newly developed analytical techniques, for the collection of more accurate data, the generation of more precise graphs, and the validation of proposed mechanisms.

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