

Radiolysis of Serine in High Radiation Field

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Abstract The formation of amino acids under simulated condition suggests that this type of compounds were readily formed on the primitive Earth. Nevertheless, there is no conclusive explanation to the origin of their specific chirality in biological systems. Differences in their stability in the primitive conditions may give some clues about this unsolved problem. Protection mechanisms have been considered, such as the adsorption of the organic compounds onto mineral surfaces. By using HPLC/ELSD to analyze aqueous suspensions of serine adsorbed on clay (sodium montmorillonite) and a meteorite (Allende) irradiated in different doses with a cobalt-60 gamma source, the aim of this work was to study the possible protector role of these mineral surfaces when an amino acid, serine, is adsorbed onto them and the system is exposed to a high radiation source. The results showed that adsorption is better at acidic pH and desorption from the mineral at basic pH. The irradiation of the free amino acid destroyed it almost completely at a dose of 91 kGy, but the presence of the mineral abruptly decreases the decomposition, acting as a protective agent. At the same time, the results in aqueous solution show no statistically significant differences in adsorption or radiolysis of D and L serine.

Keywords: Chemical evolution, adsorption, chirality, ionizing radiation.

1. INTRODUCTION

According to the hypotheses of chemical evolution, life arose following the sequence inorganic-organic-biological molecules. Two types of compounds

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Aguilar-Ovando, E.Y. that provide the foundations of life are nucleic acids and proteins. These
Negrón-Mendoza, A. molecules are very complex and formed by small units. In the case of proteins,
these are amino acids. Amino acids are essential compounds in biological
systems that are linked to almost every life process.

Serine is an essential amino acid that participates in the biosynthesis of purines and pyrimidines, which are part of the nucleic acids. It is also the precursor of numerous other metabolites and takes part in the catalytic function of many enzymes. Serine is considered prebiotic because it can be formed and detected easily in simulated prebiotic environment experiments and meteorites, and it has been identified in space [6, 8]. It presents the same homochiral condition that all biological amino acids have.

Including viruses and prions, all known biological systems present L-amino acids and D-sugars, making this an important feature to be investigated and understood to help explain the origins of life. Research in this field has involved multiple approaches to study the emergence and maintenance of homochiral systems [3, 7].

To ensure that amino acids endured in the primitive conditions, some protection mechanisms may have been enacted, such as the adsorption of the organic compounds onto mineral surfaces. Considerations have been made about preferential adsorption of species on the surfaces of crystalline minerals present in primitive times—such as calcite (CaCO_3), olivine ($(\text{Mg,Fe}^{2+})_2\text{SiO}_4$), and clays—that could have caused the concentration or stabilization of one enantiomer (one of two stereoisomers that are mirror images of each other), instead of leading to the racemic (50:50) mixture that simple chemical synthesis gives, or at least, delayed its racemization [4, 5], allowing further autocatalytic amplification processes [1].

2. METHODOLOGY

The experimental work was divided into groups of experiments: (a) adsorption tests, (b) desorption tests, (c) determination of adsorption sites, and (d) irradiation tests.

The adsorption and desorption tests (a) and (b), were performed by changes in the pH of amino acid solutions in the presence and absence of finely divided minerals, verifying the adsorption and desorption using high-performance liquid chromatography (HPLC) coupled with a scattering light detector (ELSD). Adsorption sites (c) were determined by using chemically blocked clays. Irradiation tests (d) were carried out in solution in the absence of oxygen by exposing the sample to different doses of gamma radiation from a cobalt-60 source at a fixed dose rate (216 Gy/min). The dose interval was

from 0 to 91 kGy. All glassware used was washed according to Draganič and Draganič protocol [2] for removing organic matter.

3. RESULTS AND CONCLUSIONS

3.1 Adsorption Experiments

Clay and meteorite suspensions were prepared with a 0.001 M DL-serine solution at different pH values ranging from 2 to 10. Solutions were placed into a 3D agitator for different periods of time from 5 to 120 minutes and then centrifuged to separate the supernatant. The collected portion was analyzed by HPLC/ELSD using a chiral column (Chirobiotic-T[®]) and D, L and DL-serine standards. The areas under the chromatograms were used to estimate the adsorption percentages for each enantiomer and determine adsorption curves (see Figure 1 (a) and (b)). The experiment was repeated several times, and samples were analyzed by triplicates under the same conditions.

It was observed for both minerals that maximum adsorption occurs after 40 minutes of contact between solutions and minerals. Meteorite rock showed an increased percentage of adsorption on the mineral surface, compared to that observed in clay at the same pH value.

In both cases, best adsorption occurs at pH 2 (near serine's $pK_1 = 2.21$), followed by adsorption at pH 6 (near serine's $pI = 5.68$). Within the clay, it is assumed that, at pH 2, when the serine molecule is protonated, the

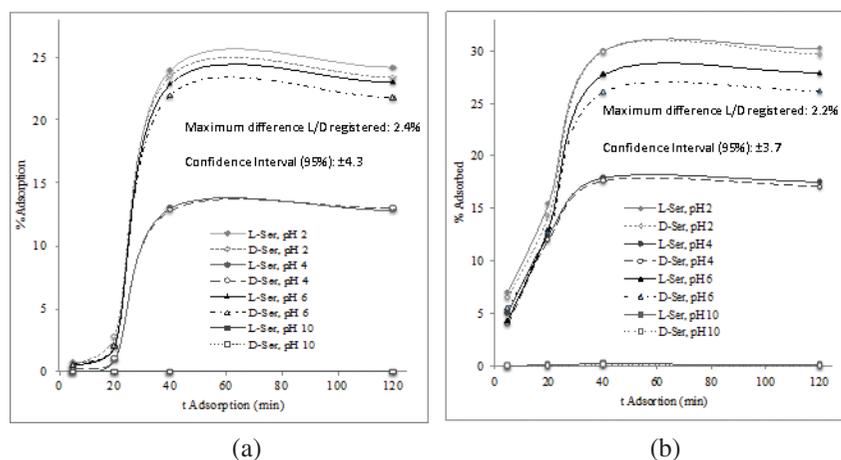


Figure 1: Adsorption curves for DL-serine onto (a) sodium montmorillonite and (b) Allende's meteorite.

Aguilar-Ovando, E.Y. adsorption occurs inside the clay's interlamellar channel by ion exchange
Negrón-Mendoza, A. (chemisorption). At pH 6, when the molecule is neutral, adsorption occurs
both inside and outside the channel by forming hydrogen bonds and weak
attractions (physisorption).

The statistical analysis of the results indicated that there is no significant difference in adsorption curves of samples, so there is no enantioselective adsorption on these two minerals.

Experiments with pretreated clays corroborate the assumption made related to the absorption sites on sodium montmorillonite (see Table 1). Clay treated with hexadecyltrimethylammonium bromide (CTAB) is channel-blocked, so when the adsorption experiment is carried out at pH 2, no serine is adsorbed (the CTAB molecule fully occupies the interlamellar channel, so no serine can get in, and no serine is adsorbed outside the channel). Clay treated with pentasodium triphosphate (Na₅P₃O₁₀) is edges-blocked, so when the adsorption experiment is carried out at pH 2, serine is adsorbed inside the interlamellar channel, as when unblocked clay is used. When the adsorption experiments are carried out at pH 6 with edges-blocked clay, there is some adsorption, indicating that at this pH value some adsorption occurs in both sites on the clay's structure.

Desorption Experiments

Desorption experiments were carried in the same way as the adsorption test, changing the pH value of solutions to extract serine from clay and meteorite where adsorption previously occurred. By using HPLC/ELSD and considering the areas under the graphics, serine desorption percentages were calculated (see Figure 2).

Results show maximum desorption (around 43%) at pH 8, followed by pH 6. This correlates to the amino acid and clay's structure as explained for adsorption. No desorption was obtained from the meteorite, indicating

Table: % of serine adsorbed onto clay treated with hexadecyltrimethylammonium (CTAB) and onto clay treated with pentasodium triphosphate Na₅P₃O₁₀.

Sample	pH	% Adsorbed	
		L-Ser	D-Ser
Serine + Clay treated with CTAB	2	0.0	0.0
	6	14.2	13.6
Serine + Clay treated with Na ₅ P ₃ O ₁₀	2	16.3	16.0
	6	7.4	7.2



Figure 2: Desorption of D, L and DL-serine from sodium montmorillonite.

that in this mineral no ionic exchange occurs; rather, a different adsorption mechanism takes place. So, the role played by this kind of mineral in the chemical evolution context should be substantially different.

Also, no statistically significant difference in desorption of samples was observed, indicating there is no enantioselective desorption from sodium montmorillonite.

3.2 Irradiation Experiments

Irradiation tests at different doses were carried out on 0.001 M solutions of racemic serine and its pure enantiomeric forms at pH 2 with cobalt-60 gamma ray source. After irradiation, solutions were analyzed by HPLC/ELSD and percentages of the serine remaining after irradiation were calculated (see Figure 3).

The experiments were performed 15 times to check the repeatability of the results. Almost total destruction of the amino acid was observed at 91 kGy. Statistical analysis of the differences between both enantiomers, as in the case of the adsorption onto clay, shows that these differences fall within the confidence interval method and therefore are not significant (there is no enantioselective decomposition).

Serine irradiation in the presence of clay, applying a dose of 91 kGy, demonstrated that the presence of mineral decreased the damage suffered by the amino acid as a result of the action of gamma radiation (see Table 2).

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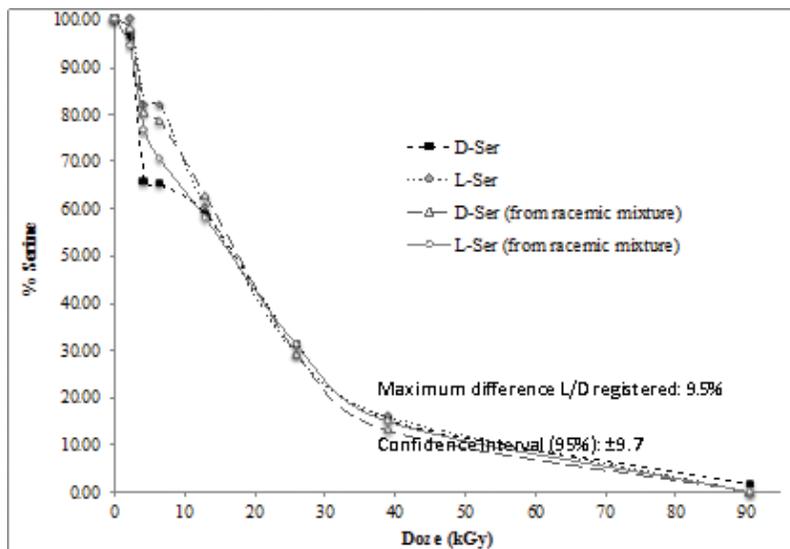


Figure 3: Decomposition curve of D, L and DL-serine when 0.001 M solutions are irradiated with gamma rays from a cobalt-60 source at pH 2.

Table: Remaining percentage of D, L and DL-serine after irradiation with a 60-cobalt gamma ray source, at pH 2, in presence and absence of clay.

Sample		% of serine after irradiation (91 kGy)	
		L-Ser	D-Ser
DL-Ser	Without clay	1.1	1.3
	With clay	66.0	69.2
L-Ser	Without clay	0.8	
	With clay	39.0	
D-Ser	Without clay		1.2
	With clay		34.6

4. REMARKS

These results confirm the capacity of concentration and protection against ionizing radiation that minerals like clay may provide to amino acids. This kind of research gives clues to a better comprehension of the chemical evolution that originated life on our planet.

Even when the differences between enantiomers in these experiments are not statistically significant, there are slight differences that may have been amplified by another mechanism, giving rise to homochirality.

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