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Computer simulation of a primitive peptide in a mineral environment analogous to the Naica system

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Abstract. Studies carried out in the cave of the giant gypsum crystals, the Naica system, discuss the possible presence of microorganisms inside them. Thus, it is important to perform computational simulations to get an insight in the possible molecular mechanisms that stabilize the organic compounds inside the crystalline lattice. These mechanisms might help to understand the preservation of organic molecules and the potential of the crystals to maintain living forms. The computational simulation in this work uses a peptide formed from the most common amino acids (in α helix and β sheet configurations) interacting with a gypsum unit cell. Our preliminary results indicate that the organic phase (α helix) is stabilized by the action of the aqueous environment. As future work, we plan to enrich the simulation of the inorganic phase, adding two more variables to the simulation (temperature gradient and ions in dissolution) to explain the mechanisms of the stability of organic compounds inside the Naica system.

1. Introduction

The Naica mine, home of the famous giant gypsum crystals ($CaSO_4 \cdot 2H_20$), has been the subject of recent studies of astrobiological importance (Perween et al. 2013). New studies detected the presence of organic matter inside the minerals, a fact that suggests that the crystal lattice plays an important role in the protection and catalysis of these molecules, some of which could be of prebiotic importance. Amino acids, the organic compounds formed by an amine (NH_2) and carboxyl (COOH) functional groups, are considered important prebiotic molecules.

Because they are precursors of proteins, it is believed they played an important role in the chemistry of the early Earth, before the first organisms arised. Glycine, the simplest amino acid has been detected in comets (Altwegg et al. 2016), a fact that suggests amino acids can form in extreme conditions, given the right conditions.

In this work we study the peptide-gypsum interaction to understand the possible role that the inorganic phase plays to improve the stability of the system, by means of 1) preserving the organic compound or 2) increasing the crystallization rate of gypsum.

Table 1. Parameters of molecular dynamics and geometry optimization

Force Field	MM+ and PM3
Time	10 ps
Step size	0.001
Cycles	20000
Temperature	273 K

2. Methodology

For the computational simulation of the organic-inorganic interaction, a hypothetical peptide was proposed, composed of glycine (Gly), methionine (Met), and glutamic acid (Gln), amino acids chosen because of its prebiotic importance (Moura et al. 2013).

The hypothetical peptide was constructed in two spatial configurations (α helix and β sheet), in order to compare the energy stability of both structures. To construct an adequate structure, the proto-biomolecule was energy optimized, utilizing molecular dynamics and geometry optimization, placing the less stable amino acids inside the peptide (to avoid structural deformations), so that the Gibbs free energy of the system had positive values.

The inorganic part of the system was the unit cell of gypsum ($CaSO_4 \cdot 2H_20$). The mineral structure was not subjected to geometry and dynamic optimization, in order to maintain its structural parameters intact.

The parameters used for the geometrical and molecular dynamics optimizations are listed in Table 1. The simulation time (referring to the time the simulated system is exposed to the desired conditions) and step size were restricted accordingly to the computational capacity available. These optimizations were carried out in four different systems (Table 2). The results of the computational simulations are reported as comparisons of theoretical Gibbs free energy and enthalpy measurements between the systems.

All computational simulations were done using the Hyperchem 8.0.1 software. The structural parameters of the gypsum unit cell were obtained from the American Mineralogist Crystal Structure Database7. The structural parameters of the amino acids were obtained from the native libraries of Hyperchem 8.0.1.

Table 2. Elements of the simulated systems

System	Description
1	Peptide
2	Peptide + Mineral
3	Peptide + Water Box
4	Peptide + Mineral + Water Box

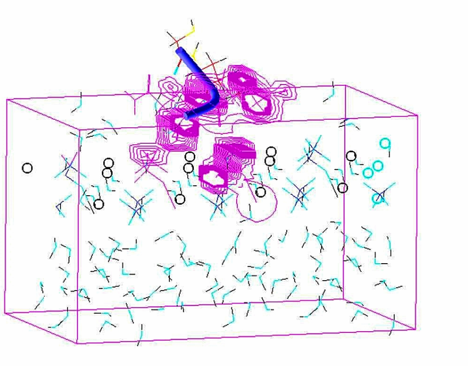

Fig. 1. Electrostatic potential map of the peptide (α helix) surrounded by a periodic box.

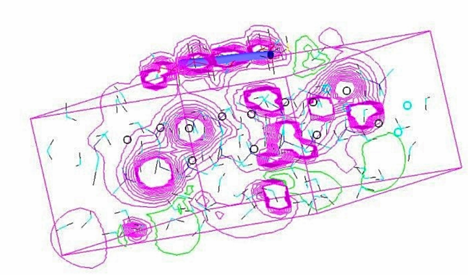

Fig. 2. Same as Fig. 1, but for the β sheet configuration.

3. Results and discussion

Table 3 reports the total energy of each simulated system. There is a clear similarity in the energy values of the two configurations, as the α helix and the β sheet both show negative values, for Systems 2–4. However, System 4 of the α helix shows the largest negative value,

Table 3. Gibbs free energy of the simulations

System	Total energy (kcal/mol)	
	α helix	β sheet
1	3.9568	3.3894
2	-7.1212	-6.5277
3	-11.5492	-21.9986
4	-387.2801	-112.0818

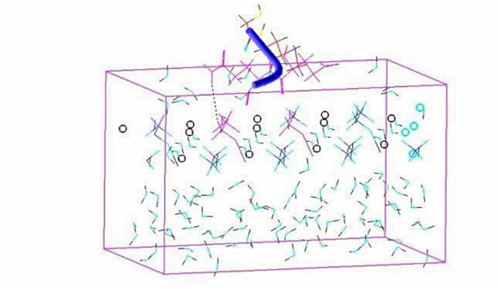

Fig. 3. Hydrogen bonding simulation for the α helix structure.

quite different in comparison to the β sheet analogue.

System 1 is the simplest, being a simulated peptide in a gaseous state (ideal model, with no interaction). Subsequent models are more complex and include a greater number of variables which make the total energy of the system to decrease. System 4 has a total energy lower than the other systems, which makes it the most plausible and the most energetically favored.

The maps of electrostatic potential for System 4 show the areas of greatest affinity between the organic and inorganic parts of the system. Figure 1 demonstrates that the α helix structure has a greater number of electrostatic interactions, relative to the β sheet (Figure 2).

The predominance of a negative charge implies affinity of the organic molecule to the mineral phase. The distribution of the electrostatic charges of the peptide allows the coupling of the charges so that there is an attraction.

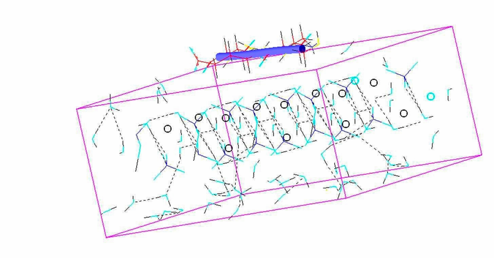

Fig. 4. Same as Fig. 3, but for the β sheet configuration.

Figure 3 shows the stability of the α helix configuration. For this structure to stabilize, hydrogen bonding must form between the organic and inorganic parts and not only in a single phase, since it destabilizes the system, increasing its free energy and reducing the plausibility of carrying out molecular interaction.

The formation of hydrogen bonding between the α helix and mineral phases increases the stability of the system. The formation of hydrogen bonds between the β sheet and the sulphate (SO_4^{2-}) ion reduces the stability of the system (Figure 4).

4. Conclusions

The simulated systems (peptide + mineral formation + aqueous environment) shows energetic stability. The Gibbs free energy of the peptides is reduced in the presence of the mineral. This fact suggests the possible formation of a chemical bond. The simulations suggest that the α helix is the most stable peptide. Future work will focus in simulating the system with a complete gypsum crystal.

References

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