

HISTIDINE SELF-ASSEMBLY AND STABILITY ON MINERAL SURFACES AS A MODEL OF PREBIOTIC CHEMICAL EVOLUTION: AN EXPERIMENTAL AND COMPUTATIONAL APPROACH

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This work describes the interaction of DL-histidine with mineral surfaces of antigorite, pirite, and aragonite. Infrared (IR) spectroscopy, Differential Scanning Calorimetry (DSC), and molecular dynamics give insight in the stability and plausible formation of peptide-like bonds between histidine molecules; mechanisms relevant in astrobiological studies.

Histidine is a key catalytic moiety in extant biological proteins, and probably fundamental in the build-up of cellular systems in prebiotic settings (Shen et al. 1990).

Slow-crystallization experiments of DL-histidine were performed in standard conditions on mineral surfaces of antigorite, pirite, and aragonite. These systems were analyzed with polarized microscopy, IR spectroscopy, and DSC, as well as computational simulations with MM+ molecular dynamics (Hyperchem).

Polarized microscopy show millimeter-sized, eu-hedral histidine crystals in the control group (Figure 1a) while histidine-mineral samples show no distinguishable histidine crystals.

IR spectra suggest the presence of peptide-like bonds in the antigorite-histidine and aragonite-histidine assemblies with the presence of amide I and amide II vibration bands (around 1700-1600 cm^{-1} and 1560-1510 cm^{-1} respectively), which were further identified with a second derivative analysis.

DSC analysis show an enhancement in histidine thermal properties in the presence of antigorite or aragonite with an increase in the decomposition temperature of histidine (275°C in antigorite and 272°C in aragonite). Moreover, computational simulations results with molecular dynamics are consistent with those of DSC, suggesting a close-distance interaction of aragonite-histidine molecules (cca. 5.5 Å) relative to the other assemblies studied (cca. 752 Å and cca.

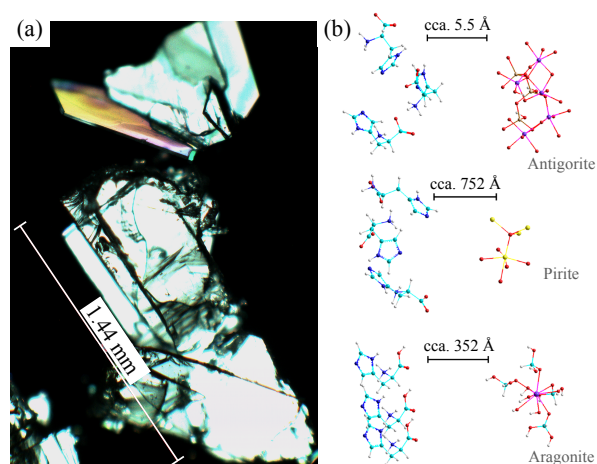


Fig. 1. (a) DL-histidine crystals, and (b) configuration of L-histidine with mineral phases after a cycle of molecular dynamics.

352 Å in pirite-histidine and aragonite-histidine assemblies respectively. See Figure 1b).

Although no crystals were observed in the mineral-histidine assemblies, IR spectra and DSC thermograms confirm the interaction between the aminoacid and their respective minerals. Peptide-like bond formation must be confirmed by other methods, since OH groups may interfere in the region of amide I/II bands. Overall, experimental and computational data support the role of mineral surfaces within a prebiotic chemistry context as catalysts and enhancers of molecular stability. Exploring the behaviour of these systems under different environmental variables (temperature, water content, pressure, radiation) might give insight into the geological settings for molecular evolution on early Earth and elsewhere in the universe.

REFERENCES

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