Adsorption and assembly of simple organics, amino acids, and sugar molecules on mineral grains in the accretion disk

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Introduction: Understanding and characterizing the underlying complex interplay between diverse organic precursors is key to answering the questions surrounding the origin of life. Specifically, we pose and address the following questions: (i) Could simple and complex organics be delivered to the early Earth via surface mediated processes such as adsorption occurring on accreting planetary grains? (ii) What would be the organic inventory of species delivered via surface mediated processes? (iii) What is the stability range (P,T) of the delivered organics? (iv) Could grain-surface mediated processes enable the synthesis and assembly of amino acids and sugars? Using density functional theory (DFT) calculations, we provide significant insights into the delivery of organics to early Earth and equally important, we show that essential organic molecules for evolution of life, such as amino acids and sugar molecules, would have been delivered endogenously to the Earth in their pristine form.

Technical Details: DFT is a robust first-principles method that provides an accurate representation of the thermodynamics and kinetics of chemical processes. Of relevance is its ability to predict adsorption energetics and reaction barriers that govern gas-mineral grain interactions. In this work, we have calculated the adsorption energetics of simple aliphatic and aromatic hydrocarbons (known to occur in the accretion disk) onto mineral surfaces (olivine, water-ice, spinel) and have catalogued their adsorption strengths. Moreover, we have studied the ability of the mineral surfaces to catalyze the formation of molecular building blocks of life (e.g., amino acids and sugars) from surface-adsorbed simpler hydrocarbons. We have analyzed these results in the context of the thermodynamic (i.e., P-T) conditions that should have prevailed in the accretion disk. These results were further utilized to rank the relative stability/volatility of the adsorbates and the subsequently produced amino acids and sugars.

All DFT calculations were carried out using VASP in a basis of plane waves [1,2]. The exchange-correlation contribution to the total energy is modelled through GGA using PBE functional [3]. The kinetic energy cutoff was set to be 450 eV and the Brillouin zone was sampled by choosing a 2×2×1 mesh of *k*-points in a Γ-centered scheme. Activation energy barriers of reactions were obtained using the nudged-elastic-band (NEB) method.

Results: In conjunction with a prior study [4] it was observed that organic molecules containing –CN, -OH, –COOH and $–NH_2$ functional groups strongly adsorb on different surfaces of olivine, magnesite, spinel and water-ice, with typical adsorption energies much greater than 1 eV (~ 100 kJ/mol). Based on their adsorption energies and alongside our equilibrium thermodynamics calculations, it can be established that at temperatures corresponding to the accretion disk, at least some, if not all, adsorbed organics containing the above functional groups should remain on the mineral surfaces. Further, it is shown that at least 10^{15} kg of organics should be incorporated into Earth as it is accreting.

Next, we examine the role of the mineral surface, the (010) facet of olivine, towards mediating the formation of a simple amino acid, namely glycine, from the –COOH- and $–NH_2$-containing building blocks. Based on the NEB method, the activation barrier for the formation of glycine on the (010) olivine surface was found to be 0.35 eV. Interestingly, the gas-phase activation barrier for formation of glycine was an order of magnitude higher (~ 3.11 eV). The noticeable decrease in the energy barrier, occurring due to the surface mediation, clearly indicates that the formation of glycine on mineral surfaces can be thermally activated. Further, once formed, the glycine molecule adsorbs strongly with a binding energy of 3.46 eV, implying that it will remain on the surface even at high temperatures. Similar trends were found for amino acids with larger molecular weight.

Finally, the formation and adsorption of sugars were studied. Trends similar to amino acids were observed for sugars (e.g., glycerol, erythrol, ribitol, glucitol), where surface mediated formation has a much lower energy barrier as compared to the equivalent gas-phase reaction. However, the typical adsorption energies for sugars are in the range of 1-1.5 eV weaker when compared to amino acids. Nevertheless, these adsorption energies suggest that sugars, once formed, would survive on mineral grains at conditions pertaining to the accretion disk.

In conclusion, it can be hypothesized that endogenous delivery of simple as well as complex organics like amino acids and sugars should be possible. In addition to aqueous alteration processes, mineral surface-mediated synthesis of amino acids and sugars represent possible pathways in the parent body and Fischer-Tropsch reaction in the protoplanetary disks.

Reference: [1] Kresse and Furthmüller (1996) Comput Mater Sci 6, 15-50; [2] Kresse and Joubert (1999), Phys Rev B 59, 1758-1775 [3] Perdew et al. (1996) Phys Rev Lett 77, 3865-3868 [4]. Asaduzzaman *et al.* (2014) EPSL, 408, 335.