A COMPUTATIONAL EXPLORATION ON THE ATTACHMENT OF ORGANICS TO MINERALS: IMPLICATIONS FOR THE DELIVERY OF ORGANICS TO METEORITE PARENT BODIES AND THE EARLY EARTH. A. M. Asaduzzaman¹, K. Muralidharan¹, K. Runge¹,², and T. J. Zega¹, ¹Material Science and Engineering, ²Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ85721. ²Quantum Theory Project, University of Florida, Gainesville, FL-32611. e-mail: asaduzzaman@email.arizona.edu.

Introduction: Carbonaceous chondrites (CCs) are among the most primitive meteoritic samples. They contain high-temperature components such as chondrules and calcium-aluminium-rich inclusions that originated in the solar nebula, presolar grains formed in ancient circumstellar environments, and low-temperature phases such as carbonates and sheet silicates that formed in asteroidal parent-bodies. The C in CC occurs in both organic and inorganic forms. Grains of presolar SiC, graphite, and nanodiamond largely constitute the inorganic C. In comparison, organic C can be categorized based on whether it is soluble or insoluble in de-mineralizing acids. The insoluble organic material (IOM) consists of a macromolecular structure that contains an abundant aromatic framework linked by aliphatic chains [1]. In contrast, the soluble organic matter (SOM) contains, e.g., carboxylic and amino acids, amides, amines, aliphatic and aromatic hydrocarbons, N-heterocycles, sulfonic acids, polyols, etc [2,3].

It is believed that the organic carbon had diverse origins including the interstellar medium, the nebular disk, and asteroidal parent bodies [1-3]. Discrete particles of IOM have been identified in CCs. Hundreds of nanometer- to micron-sized, often hollow spheres (‘nanoglobules’), in meteorites, some containing isotopic anomalies, and interpreted as having formed in the outer reaches of the solar protoplanetary disk or cold interstellar clouds[4] as well as on meteorite parent bodies. Whatever their origins, nanoglobules and other organic compounds, whether IOM or SOM, were delivered to the meteorite parent bodies, and ultimately, Earth [5]. It is unlikely that all of this material was delivered in discrete particle form but rather as films on grain surfaces. In recent studies [6], it was shown that water could be adsorbed onto various mineral surfaces and delivered to the Earth. Here we expand on that work and explore similar possibilities for organic compounds.

Computational Methods: We have performed a first-principles density-functional theory (DFT) study on the adsorption of a host of organic molecules (hydrocarbons, amine and carboxylic groups containing organic molecules) on different surfaces of olivine (MgSiO₃), water ice, magnesite (MgCO₃) and spinel (MgAl₂O₄). These materials were chosen to represent those that could have formed in a range of environments, e.g., circumstellar, nebular, and asteroidal. We chose model organic molecules such as methane, ethene, benzene, methyl amine and formic acid. Here we present the characteristics of the interaction between organic molecules and inorganics substrates.

The calculations are performed by plane-wave density-functional theory (DFT) using VASP (Vienna ab initio simulation package), version 5.2 [7, 8]. The exchange-correlation contribution to the total energy is modeled using the GGA functional of PBE. The electronic interactions are described by Projected Augmented Wave (PAW) provided by VASP. The cutoff energy for the plane wave expansion is set to 450 eV. For the number of k-points, we have used a 2×2×1 Monkhorst-Pack k-points grid for the calculations. The semi-core 2p electrons of Mg are treated explicitly.

Results and Implications: The adsorption of methane (CH₄), ethene (C₂H₄), benzene (C₆H₆), methyl amine (CH₃NH₂) and formic acid (HCOOH) is studied on three different surfaces of olivine, ice, four different surfaces of magnesite, and three different surfaces of spinel (Table 1). The adsorption energy (ΔE) of organics on different surfaces is calculated as:

\[ \Delta E = E_{\text{org/surface}} - E_{\text{surface}} - E_{\text{org}} \]

and summarized in Table 1.

Table 1: The adsorption energy, ΔE (in eV) of organics on various surfaces of forsterite, ice, magnesite and spinel.

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Surfaces</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₆H₆</th>
<th>CH₃NH₂</th>
<th>HCOOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>010</td>
<td>-0.05</td>
<td>-0.23</td>
<td>-0.26</td>
<td>-1.02</td>
<td>-0.90</td>
</tr>
<tr>
<td>Ice</td>
<td>0001</td>
<td>-0.40</td>
<td>-0.79</td>
<td>-0.61</td>
<td>-1.83</td>
<td>-1.64</td>
</tr>
<tr>
<td>Ice</td>
<td>0001d</td>
<td>-0.39</td>
<td>-0.94</td>
<td>-1.75</td>
<td>-1.84</td>
<td>-1.84</td>
</tr>
<tr>
<td>Magnesite</td>
<td>10-10</td>
<td>-0.27</td>
<td>-0.51</td>
<td>-0.35</td>
<td>-1.33</td>
<td>-1.23</td>
</tr>
<tr>
<td>Spinel</td>
<td>110</td>
<td>-0.02</td>
<td>-0.04</td>
<td>-0.02</td>
<td>-1.29/</td>
<td>-1.14/</td>
</tr>
<tr>
<td>111</td>
<td>-0.24</td>
<td>-0.34</td>
<td>-1.00</td>
<td>-1.68</td>
<td>---</td>
<td></td>
</tr>
</tbody>
</table>

It should be noted that for some systems, both pristine as well as deflected surfaces (denoted by d in Table 1) were examined. The calculated adsorption energy on all surfaces suggest that pure hydrocarbon molecules (CH₄, C₂H₄, C₆H₆) are relatively weakly adsorbed than amine and carboxylic acid containing molecules on all surfaces. This can be understood from the electronic structure of the organic molecules and sur-
faces. Pure hydrocarbons generally interact with other materials through covalent interactions. In this case, almost all surfaces contain metal (Mg, Al,) and oxygen atoms that are ionically bonded, resulting in the surfaces weakly interacting with the hydrocarbons. On the other hand, the amine and carboxylic group containing organic molecules interact strongly with the ionic surfaces through their functional groups. In particular, the strong chemisorption of the amine and carboxylic acids groups containing hydrocarbons is based on the electronegative nature of the N and O atoms. Organic compounds having similar electronegative elements in their functional groups would also strongly interact with surfaces. Thus, we can expect stable chemisorption of alcohol, aldehyde, and amide on the different surfaces studies. Further, an aliphatic tail to this functional group would also stabilize the chemisorption as they are known as electron releasing group.

In summary, the fact that some organic molecules adsorb very strongly to mineral grains characteristic of primitive meteorites, suggests that they can serve as precursors for the formation of more complex organic forms on Earth. The chemical pathways leading to the formation of the more complex organic forms is currently in progress.

**References:**