A computational investigation of adsorption of organics on mineral surfaces: Implications for organics delivery in the early solar system

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ABSTRACT

The adsorption of simple organic compounds onto minerals that are known to occur in the early solar nebula such as olivine, spinel and water-ice, is examined using first-principles density functional theory. The calculations show that electron-rich organics and organics containing cyanide, amine and carboxylic functional groups can strongly bind to low-index surfaces of olivine and spinel. Based on the surface coverage as obtained from these calculations, it can be inferred that an estimated amount of 10^{13} kg of organics could have been delivered to early Earth via direct *adsorption* mechanisms, thereby providing an endogenous source of planetary organics. In addition, adsorption of organic compounds on magnesite, a carbonate phase believed to have formed via aqueous processes on asteroidal bodies, is also studied. The adsorption behavior of the organics is observed to be similar in both cases, i.e., for minerals that formed during the earliest stages of nebular evolution through condensation (spinel and olivine) or other processes and for those that formed via hydration processes on asteroidal bodies (magnesite). These results suggest that direct incorporation via adsorption is an important delivery mechanism of organics to both asteroidal bodies and terrestrial planets.

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1. Introduction

Organic matter occurs in primitive planetary materials such as chondritic meteorites and interplanetary dust particles (IDPs). In carbonaceous chondrites, carbon can constitute up to 5 wt% (Grady et al., 2002), which occurs in both organic and inorganic forms. Grains of presolar SiC, graphite, and nanodiamond largely constitute the inorganic carbon (Gilmour, 2003). In comparison, the organic carbon can be categorized as that which is either soluble or insoluble to de-mineralizing acids. The soluble organic matter or SOM contains, e.g., carboxylic and amino acids, amides, amines, aliphatic and aromatic hydrocarbons, N-heterocycles, sulfonic acids, polyols, etc. (Gilmour, 2005; Pizzarello et al., 2006). In comparison, the insoluble organic matter (IOM) consists of a macromolecular structure that contains an abundant aromatic framework linked by aliphatic chains (Remusat et al., 2005). IDPs contain a carbonaceous matrix that can contain H and N isotopic anomalies, which infrared spectroscopic measurements suggest occur in aliphatic hydrocarbon groups linked to macromolecular networks (Keller et

al., 2004). Some of the organic matter found in carbonaceous chondrites and IDPs is believed to have originated in interstellar space or the outer reaches of the solar protoplanetary disk based in part on its isotopic composition (Messenger, 2000). Further, it is now well established from analytical studies of these planetary materials that pre-biotic organic matter and inorganic mineral grains were intimately associated in the early solar system. For example, nanoscale-size spheres that contain a core-shell microstructure, in which the shell is solid and the core hollow (so-called 'nanoglobules'), occur in carbonaceous chondrites juxtaposed with a host of inorganic mineral phases (Garvie et al., 2008; Nakamura et al., 2003). In comparison, in situ work has also revealed that organics can occur as films either between or as coatings on grain surfaces (De Gregorio et al., 2010; Zega et al., 2010). Further, chemical analysis of relatively unprocessed interplanetary dust particles (IDP) suggests that primitive solar-system material can contain large amounts of organic matter (Flynn et al., 2003; Keller et al., 2004), resulting from incorporation of organics into sub-micron planetary dust grains.

In this context, an investigation examining the nature of interactions between organic compounds and inorganic dust grains can provide a fundamental understanding of their underlying

chemistry. Insight into the mechanisms and chemical pathways that govern the delivery and incorporation of organics into planetary bodies can be obtained. Such an investigation can also shed light on the possibility of an endogenous origin of organics (i.e., whether organics were present on the early Earth as it was accreting) and ultimately, those compounds that gave rise to life on the early Earth. Here we use first-principles based density functional theory (DFT) to examine the chemical interactions between model organic compounds and inorganic substrates. In particular, we characterize and quantify the adsorption energies of organic compounds on mineral surfaces that are representative of matter present in the solar nebula, interstellar medium (ISM), and circumstellar environments (CSEs). Using this information, we examine the viability of adsorption of organics onto planetary grains in the solar nebula as a mechanism for organics-delivery, and estimate the possible amount of organic material that could have been delivered to the early Earth via adsorption. The proposed mechanism of organics delivery that involves adsorption is in addition to (i) endogenous organic sources such as organic molecules produced by ultraviolet irradiation-driven and/or electric discharge-driven reactions that occur in a reducing atmosphere (Clarke and Ferris, 1997; Miller, 1992), as well as geothermal energy driven-hydrothermal reactions (Baross and Hoffman, 1985), and (ii) exogenous sources that include interplanetary dust particles, meteorites, comets, asteroids (Anders, 1989; Chyba and Sagan, 1992) as well as impact shock-driven synthesis within the Earth's atmosphere (Chyba and Sagan, 1992).

The molecules examined in this work represent the building-blocks of more complexes organic compounds. We specifically investigate a saturated aliphatic molecule (methane), an unsaturated aliphatic molecule (ethene), an unsaturated aromatic system (benzene), as well as molecules containing functional groups such as methyl-amine, methyl-cyanide and formic acid, which are known to exist in the solar nebula as a result of presolar synthesis (Pizzarello et al., 2006). The modeled inorganic host materials include various low-index surfaces of olivine, water ice, and spinel. Olivine and spinel occur in various components of primitive chondrites, e.g., chondrules and calcium–aluminum-rich inclusions (MacPherson, 2004; Papike, 1998), which are believed to have formed in early nebular environments. We also examine the adsorption of the chosen organic compounds on magnesite surfaces. Magnesite is representative of minerals that were formed via aqueous alteration on the parent bodies of primitive chondrites (Brearley, 2006; Buseck and Hua, 1993; Zolensky et al., 2002). By investigating the chemistry of interactions of organic compounds with these materials, our goals are to (1) investigate the efficacy of adsorption as a mechanism for delivering organic matter to the parent asteroids of meteorites; and (2) establish a hierarchical classification of organic compounds that could bind strongly to the inorganic substrates incorporated into the planetary building blocks during the early stages of planetary accretion.

2. Computational methods

Calculations have been performed using the plane-wave code VASP (Vienna *ab initio* simulation package), version 5.2 (Kresse and Furthmüller, 1996; Kresse and Joubert, 1999). The exchange-correlation contribution to the total energy is modeled using the generalized gradient approximation (GGA) functional of Perdew–Burke–Ernzerhof (PBE) (Perdew et al., 1996) and as needed, long-range corrections are employed using the DFT-D2 semi-empirical method (Grimme, 2006) for molecules such as benzene and ethene, which demonstrate significant polarization effects when interacting with mineral-surfaces. The electronic interactions are described by the Projected Augmented Wave (PAW) method (Blöchl, 1994; Kresse and Joubert, 1999) that incorporate scalar

relativistic corrections as provided by VASP (Kresse and Hafner, 1994). The cutoff energy for the plane wave expansion is set to 450 eV. A $2 \times 2 \times 1$ Monkhorst–Pack (Monkhorst and Pack, 1976) k-points grid is used in our calculations. The semi-core $2p$ electrons of Mg are explicitly treated. All calculations are performed in a periodically repeated simulation supercell and a vacuum space of 15 Å while simulating the different mineral surfaces to prevent spurious interactions between periodic surface slabs. A convergence criterion that ensures all atomic forces be smaller than 0.02 eV/Å was imposed while locating energy-minimized bare and adsorbed surfaces. For both bare and adsorbed surfaces, atoms forming the bottom layer of the slab are kept in their bulk positions. All other atoms are allowed to relax. The construction and size of the supercell of different adsorbents is discussed in the respective sections below. We note that a similar computational methodology was used to successfully characterize the adsorption of water molecules onto mineral surfaces and thereby provide new knowledge on the accretion-disk origin of planetary water (Asaduzzaman et al., 2012a, 2013; Asaduzzaman and Muralidharan, 2012; de Leeuw et al., 2010; Muralidharan et al., 2008; Prigiobbe et al., 2013; Stimpfl et al., 2006; Vattuone et al., 2013). Further, to the best of our knowledge, this is the first study which deals with quantification of organics that can be delivered to the early Earth via adsorption.

3. Results and discussion

The adsorption of methane (CH_4), ethene (C_2H_4), benzene (C_6H_6), methyl cyanide (CH_3CN), methyl amine (CH_3NH_2) and formic acid (HCOOH) is studied on the most energetically stable, low-index surfaces of olivine, water ice, magnesite, and spinel. In order to locate the most stable adsorption configuration, the surface is divided into a 0.25 Å $\times 0.25$ Å grid. The adsorption of the organic molecule at each grid-site is examined via a geometry optimization procedure and the configuration corresponding to the lowest adsorption energy geometry is selected. Typically, for the adsorption of organics onto the mineral surfaces, there are many favorable sites that are available for adsorption. The adsorption energy, ΔE of organics on different surfaces is calculated as:

$$\Delta E = E_{org/surface} - E_{surface} - E_{org},$$

where $E_{surface}$ is the energy of the surface, E_{org} is the cohesive energy of the organic molecule and $E_{org/surface}$ is the energy of the surface along with the adsorbed organic molecule. A negative ΔE signifies stable adsorption. For the sake of simplicity, we refer only to the numerical values of adsorption energy in the text. It is noted that we restrict our calculations to characterizing the adsorption of a single molecule on the respective surfaces and consequently the reported adsorption energies are in units of eV per molecule. Based on the strength of adsorption, the interactions between the organic compounds and the respective surfaces are classified to be either (i) *weak*, where physisorption occurs, (ii) *intermediate*, where the molecules are moderately polarized in the presence of the surface, and (iii) *strong*, where the molecules chemisorb via formation of ionic bonds with the surface or are significantly polarized in the presence of the surface leading to significant distortions in the molecular-configuration.

Below, we discuss the surface morphology of the different mineral-systems under study and then focus on the different molecules and their interactions with the surfaces. All surfaces were created by cleaving a supercell (i.e., periodically repeated unit-cell) of the most-stable bulk polymorph.
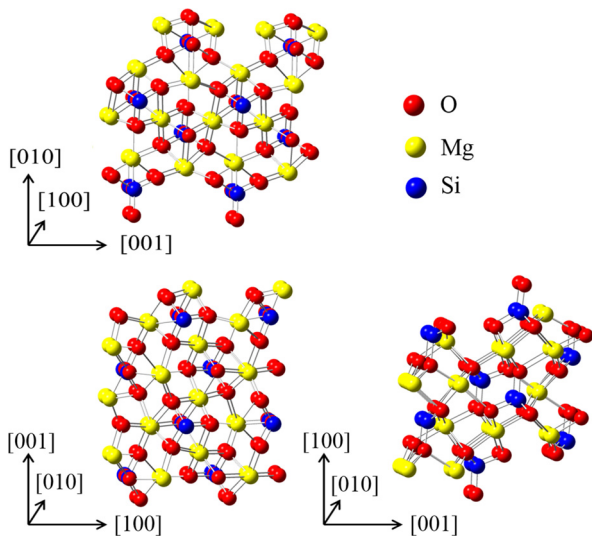
Fig. 1. A side-view of different olivine (010), (001) and (100) surfaces. The topmost atoms are surface atoms. Note the singly-coordinated oxygen atoms on the (100) surface.

3.1. Surfaces

3.1.1. Olivine (Mg₂SiO₄)

Three surfaces (100), (010) and (001), of forsterite (i.e., the Mg-end member of olivine) were examined in this study (Fig. 1). The surfaces were created by keeping the fundamental SiO_4 polymeric unit of the bulk olivine intact, consistent with the methodology proposed by de Leeuw et al. (2000). The modeled olivine consists of a (2×2) supercell containing 112 atoms. A detailed description of the structural characteristics of the different surfaces of olivine can be found in Asaduzzaman et al. (2013) but we note that all surfaces consist of undercoordinated Mg and O atoms. The number density of surface Mg atoms on the (100) and (010) surfaces is twice the number density on the (001) surface.

3.1.2. Water ice

The (0001) ice surface is created by cleaving an optimized bulk hexagonal-ice polymorph (Ih) periodic cell. A (2×2) supercell containing five bilayers (120 atoms) was chosen for the calculation based on the investigations of Asaduzzaman and Schreckenbach (2010), Asaduzzaman et al. (2012b). The (0001) surface of ice contains both hydrogen and oxygen atoms, but, unlike olivine, the surface atoms are not undercoordinated. A depiction of the ice-surface is shown in Fig. 2.

3.1.3. Magnesite (MgCO₃)

Two low-index magnesite surfaces, namely, (0001) and (10$\bar{1}$0) have been considered in this work as shown in Fig. 3. Both (3×3) and (2×3) supercells containing 270 and 240 atoms are chosen to represent the (0001) and (10$\bar{1}$0) surfaces respectively. The (0001) surface is characterized by the presence of undercoordinated Mg atoms, while the (10$\bar{1}$0) surface contains both undercoordinated Mg and O atoms.

3.1.4. Spinel (MgAl₂O₄)

Three low-index spinel surfaces, namely, (001), (110) and (111) were considered in this work. All surfaces were modeled as (2×2) supercells, each containing 112 atoms. Depending on the method of cleavage, the (111) surface was either terminated with Al or O atoms. The Al-terminated surface is energetically more stable, and henceforth we only use the Al-terminated surface in our study. In contrast, both (001) and (110) surfaces have undercoordinated Mg
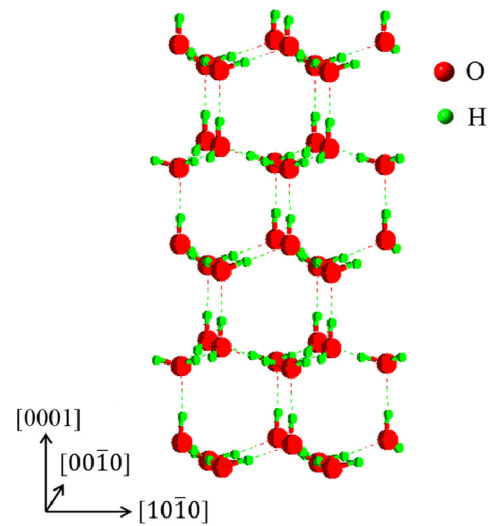
Fig. 2. Side-view of the (0001) surface of ice.
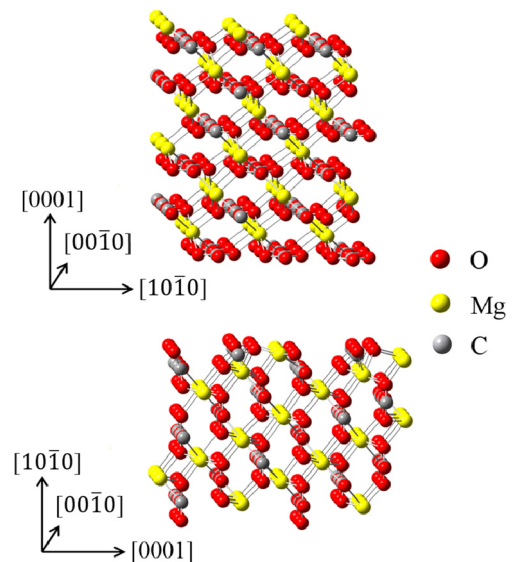
Fig. 3. Side view of magnesite (0001) and (10$\bar{1}$0) surfaces.
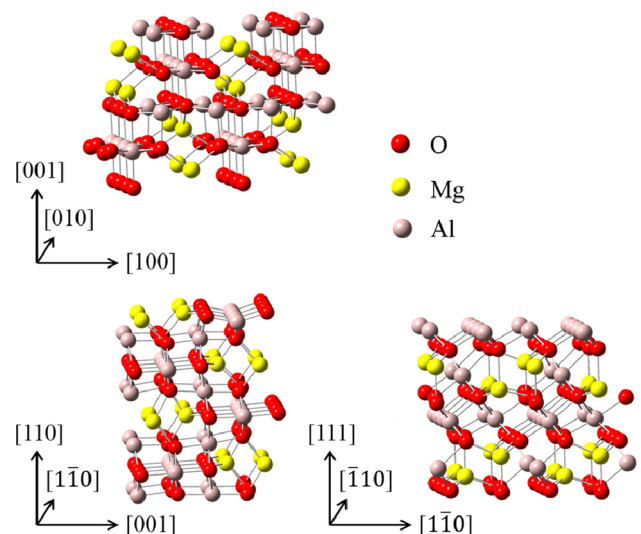
Fig. 4. Side view of spinel (001), (110) and (111) surfaces.

Table 1
The adsorption energy, ΔE (in eV) of organics on various surfaces of olivine, ice, magnesite, and spinel. (−) denotes dissociation of the molecule on the given surface.

Materials	Surfaces	Organics					
		CH_4	C_2H_4	C_6H_6	CH_3CN	CH_3NH_2	$HCOOH$
Olivine	010	−0.05	−0.52	−0.87	−0.88	−1.02	−0.90
	100	−	−1.15	−1.40	−1.35	−	−1.40
	001	−0.40	−0.99	−1.31	−1.53	−1.83	−1.64
Ice	0001	−0.10	−0.19	−0.27	−1.01	−0.66	−0.66
Magnesite	0001	−0.39	−1.17	−2.30	−1.84	−1.84	−1.84
	10$\bar{1}$0	−0.27	−0.66	−0.71	−1.01	−1.33	−1.23
Spinel	001	−0.03	−0.32	−0.59	−1.10	−1.29	−1.14
	110	−0.02	−0.30	−0.59	−1.04	−1.29	−1.20
	111	−0.24	−0.73	−2.59	−1.53	−1.68	−

and Al cations and O anions. However, the ratio of Al to Mg is different for the two surfaces; in the (001) surface, the Al/Mg ratio is 2, whereas that for the (110) is 1 (Fig. 4).

3.2. Organics adsorption

3.2.1. Methane

Methane (CH_4) represents the simplest saturated hydrocarbon, where the central carbon atom is covalently bonded to four hydrogen atoms. In the case of the olivine (100) surface, the methane molecule is destabilized in the presence of singly coordinated oxygen atoms, leading to its dissociation. An olivine surface O atom becomes hydroxylated while the resulting CH_3 group bonds to another surface O. In comparison, methane physisorbs on all other olivine surfaces, with the resulting adsorption energy being <0.25 eV (see Table 1).

3.2.2. Ethene

Ethene (C_2H_4), which represents the simplest unsaturated aliphatic hydrocarbon, is an electron-rich molecule and consequently, its adsorption on each surface under study, is largely determined by the strength of the electrostatic interactions between the delocalized pi-electrons (within the ethene molecule) and the surface atoms. In particular, the presence of electropositive surface atoms (i.e. cations) enhances adsorption, while the presence of electronegative surface atoms (i.e. anions) decreases the strength of adsorption. Further, the charge-density of the surface-atoms is dependent on their coordination, and larger charge-densities are especially associated with undercoordinated cations as compared to their coordinated counterparts. The interplay between the above-identified properties determines the strength of adsorption; in particular, olivine (100) and magnesite (0001) surfaces demonstrate the strongest adsorption (Table 1), which can be attributed to the sole presence of undercoordinated surface Mg atoms. The attractive Coulomb interaction between the ethene molecule and the surface Mg atom leads to the strengthening the adsorption of ethene. In contrast, for example, in the case of magnesite (10$\bar{1}$0) surface, the additional presence of surface O atoms diminishes the adsorption strength due to mutual repulsion between the O atoms and ethene.

3.2.3. Benzene

Benzene (C_6H_6), the simplest aromatic hydrocarbon examined in this study, is characterized by the presence of six pi-electrons per molecule and is thus highly polarized in the presence of surface cations. This polarization results in stronger adsorption as compared to ethene for all surfaces. Further, the extent of polarization in the benzene molecule is reflected by the level of distortion in the benzene-geometry, as seen for substrates that are predominantly characterized by the presence of undercoordinated cations, e.g., spinel (111) and magnesite (0001). This distortion is illustrated in Fig. 5 for benzene adsorption on spinel surfaces.
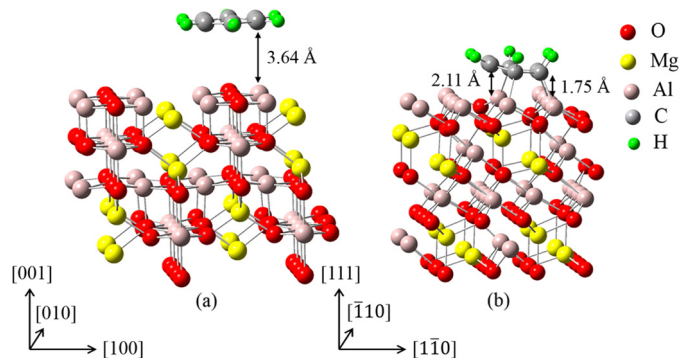
Fig. 5. Optimized adsorption geometry of benzene on (a) (001) and (b) (111) surfaces of spinel. Note the significant distortion (loss of planarity) of the benzene molecule in (b) and the difference in adsorption distance between the benzene molecule and the respective surfaces.

3.2.4. CH₃CN (methyl cyanide)

The –CN functional group determines the adsorption characteristics of methyl cyanide, leading to the formation of strong ionic bonds with the surface cations present on the various substrates. Specifically, the presence of the lone-pair of electrons on the N atom facilitates the bond formation with surface cations, e.g., Mg atoms, which are present on all surfaces studied herein except for ice. Also, the ionic-bond formed between –CN and surface Mg atoms in spinel is much stronger than the bond formed between the –CN and surface Al atoms. In contrast, methyl cyanide interacts weakly with the ice-surface, via the formation of weaker hydrogen bonds.

3.2.5. CH₃NH₂ (methyl amine)

The adsorption characteristics of methyl amine are driven by the presence of the N atom in the –NH_2 functional group, and thus the observed trends for both methyl amine and methyl cyanide are similar. Nevertheless, the presence of the two H atoms enables the formation of H bonds with surface O atoms, leading to some differences in the adsorption energies when compared to methyl cyanide. Interestingly, in the case of ice, methyl amine adsorbs more weakly as compared to methyl cyanide; this is due to the (i) planar nature of the surface, which restricts the formation of H bonds for the methyl amine system and (ii) presence of 2π-electrons in the –CN group that enables stronger polarization effects. In comparison, methyl amine dissociates on the olivine (100) surface. An H atom, belonging to the amine functional group, binds to the singly coordinated surface oxygen, leading to dissociation.

3.2.6. HCOOH

The simplest carboxylic acid, namely, formic acid (HCOOH), contains a highly electronegative O atom, similar to the N atom in –NH_2 and –CN functional groups of methyl amine and methyl
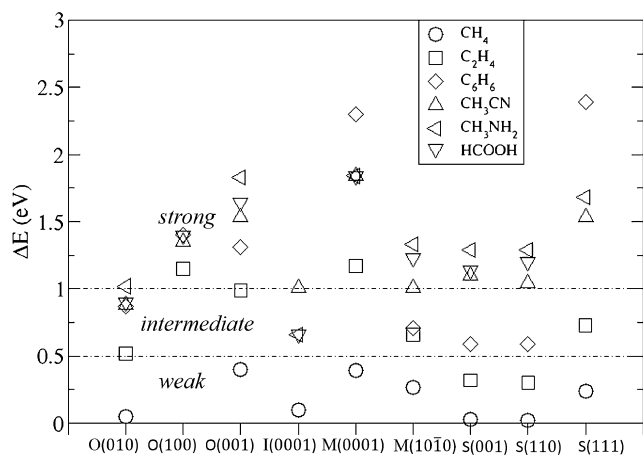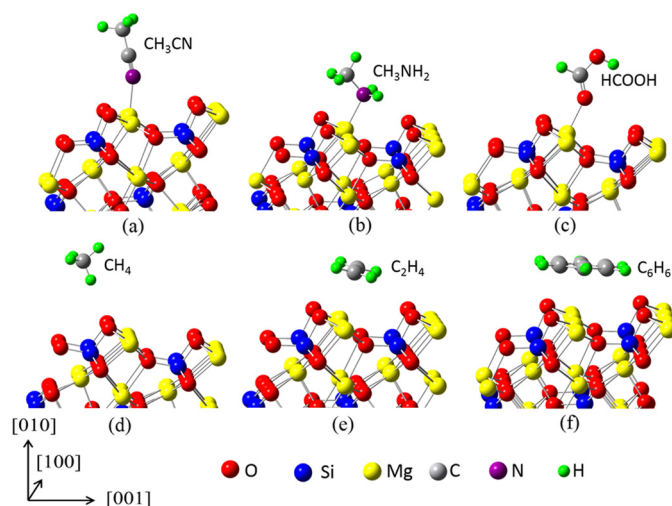
Fig. 6. Adsorption energies of organics on various mineral surfaces. O, I, M, and S represent olivine (O), water-ice (I), magnesite (M) and spinel (S). While the adsorption energies are negative, for simplicity we only report the absolute value of the adsorption energies.

Fig. 7. The stable adsorption configuration for (a) methyl cyanide, (b) methyl amine, (c) formic acid, (d) methane, (e) ethene, and (f) benzene on the (010) surface of olivine. For the sake of clarity, only atoms close to the surface are shown in the figure. Note the strong chemical bonds between the respective surfaces and the N/O of organics in (a)–(c), while the organics depicted in (d)–(f) are physisorbed onto the surface. The atom types are color-coded as shown in the figure.

cyanide. The similar polarity leads to comparable trends among the carboxylic, methyl amine, and methyl cyanide molecules. An exception is that formic acid dissociates on the spinel (111) surface. Specifically, the OH group chemically attaches to a surface Al atom, leading to dissociation.

4. Cosmochemical implications

The strength of adsorption of the organic compounds under study with the various mineral surfaces is summarized in Fig. 6, and their adsorption geometries on olivine (010) are shown in Fig. 7. The stable adsorption geometries of all other molecules on all other surfaces can be found in Electronic Supplement. Based on the adsorption energies, when viewed in conjunction with the work of Muralidharan et al. (2008), we have classified the interactions to be weak, intermediate or strong, where strong binding indicates that adsorption is stable even at high temperatures ($\sim$1200 K). In particular, Muralidharan et al. (2008) using kinetic Monte Carlo simulations in conjunction with adsorption energies as calculated from atomistic simulations, demonstrated that when the adsorption energy of water molecules was greater than 1 eV, they could be retained on olivine surfaces even at temperatures equaling 1200 K. From Fig. 7, it is clear that functional groups containing electronegative elements help in strongly binding the organics to the mineral surfaces. In addition, compounds that are unsaturated and therefore electron rich also bind strongly to certain surfaces. In light of these observations, we should expect that stable chemisorption of unsaturated hydrocarbons as well as alcohol-, aldehyde-, and amide-containing compounds on minerals occurred in multiple environments including circumstellar, interstellar, and the early solar nebula. Radioastronomical observations have shown a wide range of organic compounds occur in cold molecular clouds (Adande et al., 2013) within the interstellar medium and evidence of the preservation of such molecules is provided by meteorites. Specifically, the carbonaceous chondrites (CCs) contain a host of organic compounds, some of which have retained a record of interstellar chemistry. The insoluble organic matter within CCs retains localized (nm) anomalies of deuterium (D) and ^{15}N that are believed to reflect preservation of presolar molecules formed in interstellar clouds or at the edge of the solar protoplanetary disk (Alexander et al., 1998; Alexander et al., 2007; Busemann et al., 2006; Floss and Stadermann, 2009; Messenger, 2000; Remusat et al., 2009; Robert and Epstein, 1982). As noted above, some of the isotopically anomalous IOM occurs in

the form of discrete particles, i.e., nanoglobules (Garvie et al., 2008; Nakamura et al., 2003), whereas other IOM occurs in the matrices of CCs interstitial to grains and as film-like coatings on them (De Gregorio et al., 2010; Zega et al., 2010), the latter suggesting the possibility of adsorption as a viable mechanism for the delivery of organics into the solar system.

We also hypothesize that chemisorption played a role in delivering organics to the parent asteroids of meteorites and the terrestrial planets. Gas–solid reactions in the solar nebula are believed to have played a prominent role in the formation of planetary materials, e.g. sulfides and oxides (Hong and Fegley Jr., 1998; Lauretta et al., 1997), and so it is plausible that organic–inorganic reactions occurred in such environments (Tielens, 2005). With respect to those compounds modeled here, alcohol, aldehyde, and amide are highly volatile, and so their condensation might be expected to have occurred beyond the snow line, hypothesized to have occurred between 2 and 4 AU. However, our calculations suggest that adsorption can be stable at temperatures approaching 1200 K, which is modeled to have occurred within 1 AU of the sun (Cameron, 1995; Lewis, 1974; Willacy et al., 1998). It is conceivable, therefore, that organics could have adsorbed onto high-temperature refractory objects, possibly even chondrules and calcium–aluminum-rich inclusions, which are believed to have formed close to the sun (Shu et al., 1996). Thus, chemisorption could have been a viable mechanism through which organic compounds were also delivered to the parent bodies of meteorites and by extension, the terrestrial planets.

Given the above discussion on the possibility of adsorbing various chemical species onto dust grains in the solar nebula, it is worth exploring how much of these materials could have been delivered, either to meteorite parent bodies or the Earth, via adsorption. We follow the method described in Muralidharan et al. (2008), and similarly we make the following assumptions: (i) 65% of Earth is made up of silicate and oxide grains (Weisberg et al., 2006); (ii) for simplicity we assume these grains are compositionally similar to olivine and are sub-micron ($\sim$0.6 µm) in size (Weidenschilling, 2000) consistent with the planetary dust grain-sizes during the early stages of planetary accretion in the solar nebula; (iii) for each grain, the surface coverage is restricted to 1 molecule/nm^2 (i.e. other stable adsorption sites within the 1 nm^2 are not considered); and (iv) the molecular weight of the

adsorbing compound is set to be 50 g (averaged over the strongly adsorbing molecules' molecular weight). Using the above data, we estimate the total surface area available for adsorption to be 2.6×10^{26} cm^2, from which we estimate the amount of simple organics that would have strongly adsorbed to be of the order of 10^{13} kg. The estimated number represents an approximation since (a) only monolayer coverage on the grains is considered and (b) the effect of grain-grain impact and its effects on organic volatility and shock-synthesis of complex organics are ignored. Further the effect of co-adsorption of other molecules is not taken into account, which may affect the adsorption strengths of the organic compounds considered in this work. Nevertheless, given the fact that most of these molecules chemisorb on mineral surfaces via formation of strong ionic bonds, we can expect that some of the adsorbed organics would survive at high temperatures as well as high-energy impact processes.

Assuming the time scale associated with the final accretion of rocky planets such as Earth to be approximately 10^7 yr (Weidenschilling, 2000), we can, on an average, estimate the rate of organic delivery to early Earth via adsorption to be 10^6/yr. This estimate is comparable to other endogenous contributions to the organic inventory on early Earth such as organic molecules produced by reactions mediated either by ultraviolet irradiation or electric discharge or atmospheric shocks, all of which range from 10^7–10^{11} kg/yr under a reducing atmosphere, to 10^1–10^8 kg/yr under a neutral atmosphere (Chyba and Sagan, 1992). In addition, exogenous sources such as IDPs, airbursts, comets and meteorites are also known to contribute similar amounts of organics (Chyba et al., 1990; Flynn et al., 2003). Also, the nature of organic compounds identified in IDPs and in meteorites (Gilmour, 2005; Keller et al., 2004; Pizzarello et al., 2006) is consistent with our observations regarding the stability of adsorbed organics on the mineral grains.

Based on these estimations, it is evident that organics adsorption on mineral grains could have been a viable mechanism for accounting for a part/significant fraction of the initial terrestrial organic inventory and thus the abiotic precursors for early life (Anders, 1989; Asaduzzaman et al., 2014; Cleaves et al., 2008; Miller, 1992; Munoz Caro et al., 2002; Nuth III et al., 2008). We note that these calculations are based on simple molecules. These small molecules are likely precursors for the formation of more complex organic compounds and macromolecules through surface mediated catalytic reactions. For example, amino acids can be a direct product of surface catalysis of adsorbed amine and carboxylic acid compounds.

5. Conclusion

Adsorption of organic molecules on surfaces of minerals that formed in varied pre-terrestrial environments, e.g., circumstellar environments, the interstellar medium, the early solar nebula, and the parent asteroids of meteorites, was investigated using first-principles density-functional-theory calculations. The results suggest that saturated hydrocarbon molecules weakly adsorb on most mineral surfaces, while they dissociate on surfaces containing a high density of oxygen-anions. In comparison, the calculations show that cyanide, amine, and carboxylic-containing compounds as well as unsaturated hydrocarbons interact strongly with all mineral surfaces via the surface metal atoms. Therefore, cyanide-, amine-, carboxylic-acid containing organics and unsaturated hydrocarbons should have been accreted by the early Earth from inorganic grains that adsorbed these materials directly. Further, the incorporation of organics within asteroidal bodies could have proceeded via direct adsorption too.

Using the energetics of adsorption for the strongly bound compounds, we have calculated the amount of endogeneous organic matter that could have been delivered through this process to be of the order of 10^{13} kg. Interestingly, this parallels the estimations of Chyba et al. (1990), who have demonstrated a comparable amount of exogenous organics should have been delivered via cometary bombardment. Also, (Flynn et al., 2003) have calculated the amount of exogeneous organics that were delivered via IDPs to be at least 15 tons per year, which when extrapolated over a few billions of years, yields comparable numbers as well. We note that the estimates made in this work are based on simple molecules. However, their chemisorption onto mineral surfaces is likely a catalytic pathway for the formation of more complex organic compounds and macromolecules, which could have astrobiological implications for the early Earth and possibly even extrasolar planets.

Acknowledgements

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.10.029.

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