Hydrocarbon adsorption on Carbonate and Silica surfaces: a First Principles study with van der Waals interactions

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We study the adsorption of hydrocarbon molecules on carbonate minerals and silica surfaces by means of first-principles calculations based on Density Functional Theory (DFT) with and without van der Waals (vdW) corrections. The inclusion of vdW corrections in ab-initio methods can improve the description of these systems particularly, the long range weak dipole-dipole interaction as well as provide a fully electronic description for the interface of hydrocarbon molecules and mineral surfaces. To take into account the vdW dispersion forces, we used the DFT with the Dispersion-Corrected Atom-Centered Potentials model (DCACP) [1] Energetic, electronic, structural and kinetic properties have been determined for the adsorption of the representative hydrocarbons (benzene, anthracene, naphthalene, toluene, heptane and hexane) on calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] (10-14) and quartz (SiO_2) surfaces. Our results suggest that Ca sites are the most energetically favorable for hydrocarbon adsorption on both carbonate systems. The calculations also indicate a weak interaction between the hydrocarbon with the bare silica surface for all hydrocarbons studied. The vdW corrections strengthen the hydrocarbon-surface bond with a corresponding reduction in the bond distance between the benzene and the surfaces. The inclusion of London dispersion forces to benzene results in an increase of 70% in the surface-molecule energy interaction. The energy barrier, for the displacement of the hydrocarbons along the calcite and quartz SiO_2 surfaces were determined using the Nudged Elastic Band method, and adsorption energies for the most stable sites show the same order of magnitude. The highest energy barriers associated with the hydrocarbon displacements on the surfaces are of the same order of the adsorption energies for the most stable sites. By taking into account the vdW interactions within the energy barriers in complement to adsorption energies in a model for hydrocarbons/mineral-rocks interaction can give us a more realistic description to the hydrocarbon carbonate/silicate interactions.
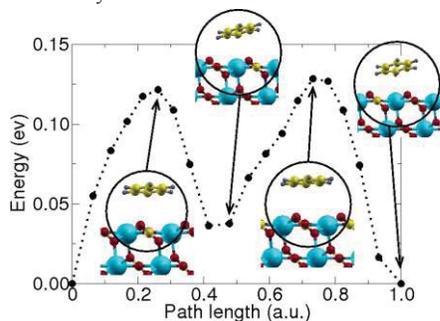

Figure1 - Energy barriers for benzene displacement along [48-1] direction for calcite (10-14) surface
[1] Lin et al. (2007) *Phys. Rev. B* **75**, 205131

Litho-, chrono- and S-MIF-chemo-stratigraphy of late Archean Dharwar Supergroup, south India

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Earth's tectonic and climatic systems may have fundamentally changed through the late Archean period, which is characterized by major deposition of banded iron formation (BIF) and appearance of stromatolite reef along continental margins. Also, mass-independent fractionation of sulfur isotopes (S-MIF) demonstrated that Earth's atmosphere and ocean were virtually oxygen-free before 2.3 Ga [1]. In the late Archean, the S-MIF signature changed dramatically: minimam $\Delta^{33}S$ at around 2.9 Ga, subsequent large $\Delta^{33}S$ variation culminated at 2.5 Ga and its sudden drop at the end of Archean. These changes may reflect perturbation of atmospheric chemistry. However, almost the S-MIF record so far came from Pilbara and Kaapvaal cratons, that may have been a single continent (Vaalbara) at that time [2], and thus the observed S-MIF may possibly reflect local environment. It is important to test the "globalism" of the S-MIF signature for tracing the atmospheric evolution.

We studied late Archean volcano-sedimentary sequence of the Dharwar Supergroup, distributed in the Chitradurga schist belt, western Dharwar craton. Our new field mapping and zircon U-Pb dating allows us to reconstruct detailed lithostratigraphy. The lower unit (post-3.0 Ga) consists of basal conglomerate, stromatolitic carbonate, silici-clastics with diamictite, chert/BIF and pillowed basalt in assending order, all of which are older than 2676 Ma magmatic zircon ages from dacite dyke intruded into the topmost pillowed basalt. The upper unit unconformably overlies the pillow lava, and consists of conglomerate/sandstone with ~ 2600 Ma detrital zircons, komatiite lava, BIF and silici-clastic sequence with mafic volcanics. Sulfur isotope analysis of extracted sulfide of these sedimentary rocks show a clear $\Delta^{33}S$-$\Delta^{36}S$ correlation with a $\Delta^{36}S/\Delta^{33}S$ slope of -0.98. This trend is similar to those reported from Pilbara-Kaapvaal equivalents, thus could be a global signature, whereas $\delta^{34}S$-$\Delta^{33}S$ relation from each stratigraphic level shows somewhat different trend, possibly reflecting local environment and/or postdepositional overprint.

 [1] Farquhar (2000) *Science,* **289,**756-758. [2] de Kock et al. (2009) *Precambrian Res.* **174**, 145-154.