Adsorption of pollutants on silicate surfaces from aerosols by computational geochemistry

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Carbonyl and heterocyclic compounds are directly emitted into the troposphere from biogenic and anthropogenic sources. The reactions of hydroxy free radicals with volatile organic pollutants are common in the troposphere [1]. Silicates and clay particles are present as components of atmospheric aerosols. Heterogeneous reactions of atmospheric gases on aerosol particles play an important role in atmospheric chemistry. Although dust particles are abundant in the Earth's atmosphere, however the kinetics and adsorption mechanisms for these reactions are not well understood.

Quantum mechanics methods based on Density Functional Theory are used to study the adsorption of thiophene on a crystal surface of pyrophyllite and the hydrogen abstraction reaction of OH free radicals with linear-chain aldehydes adsorbed on models of silicate surfaces by using $(SiO_4)_n$ cluster models [2] and a crystal structure of pyrophyllite [3]. We find that the silicate surface is a good quencher of free radicals and aldehydes, adsorbed on the silicate surface, can react with OH free radicals to yield surface-bound formyl radicals and water. The presence of silicate surface does not change significantly the activation energy and theoretical kinetic studies show that this reaction is less favored on the silicate surfaces than in gas phase.

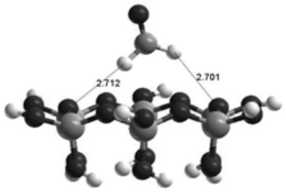

Figure 1: Formaldehyde adsorbed on silicate surface model.

[1] Alvarez-Idavoy *et al*. (2001) *J. Am. Chem. Soc.* **123**, 2018. [2] Iuga *et al*. (2008) *J. Phys. Chem. C* **112**, 4590-4600. [3] Sainz-Díaz *et al*. (2002) *Am. Mineral.* **87**, 958-965.

Strategies for economization of iron in *Crocosphaera watsonii* as revealed by global proteomic analyses

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Crocosphaera watsonii is a diazotrophic cyanobacterium found in tropical ocean environments and is considered one of the major contributors to marine nitrogen fixation. These oligotrophic marine environments are often extremely depleted in nutritive trace elements such as iron and cobalt. The high requirement of iron in the nitrogenase complex poses questions about how this organism can sustain its required cellular iron quota. The iron and molybdenum cellular quotas have previously been observed to double at night when nitrogen fixation is known to occur in this microbe (Tuit *et al*., 2003). Using mass spectrometry based global quantitative proteomic analysis we clearly demonstrate the synthesis of the three iron containing proteins from the nitrogenase complex during the dark period followed by their complete degradation during the photoperiod. Similarly flavodoxin is also synthesized only during the dark period, suggesting it is the enzyme responsible for electron transfer to nitrogenase in *Crocosphaera*. These results point to a portion of the iron cellular quota that is dynamic, being used for both photosynthesis and nitrogen fixation during different times of the day in order to optimize iron use efficiency. The implications for the development of proteomic geochemical biomarkers will also be discussed.