Photocatalytic Properties of Minerals and their Role in Prebiotic Chemistry

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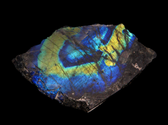
A myriad of astrophysical environments, once thought to be barren of anything but hydrogen and helium, are now known to be rich in complex carbon chemistry. Not only are carbon molecules such as amino acids and polycyclic aromatic hydrocarbons (PAHs) present in interstellar space, but also on the rocky bodies of our Solar System, as confirmed by the species found in the Murchison and other meteorites. When these organic molecules are adsorbed to their mineral substrates, they undergo a different chemical evolution than they would in gas phase. The resulting reactions play a part in generating organic species important to the inventory of prebiotic chemistry on the early Earth, Mars, asteroids, and comets. In this PhD project, we specifically focus on photocatalysis: how iron and magnesium bearing minerals act as catalysts to accelerate the destruction of PAHs by radiation. Here, we present preliminary data of pilot experiments using glycine. Glycine is a very well studied organic compound and therefore excellently suited as a test molecule to begin designing the experimental approach.

Early Solar System minerals[1]

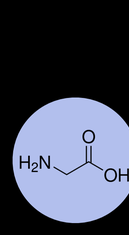


gabbros ex. labradorite

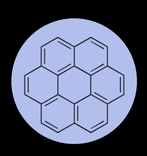
silicates ex. forsterite

iron oxides ex. magnetite

Organic molecules found in meteorites



amino acids ex. glycine



PAHs ex. coronene

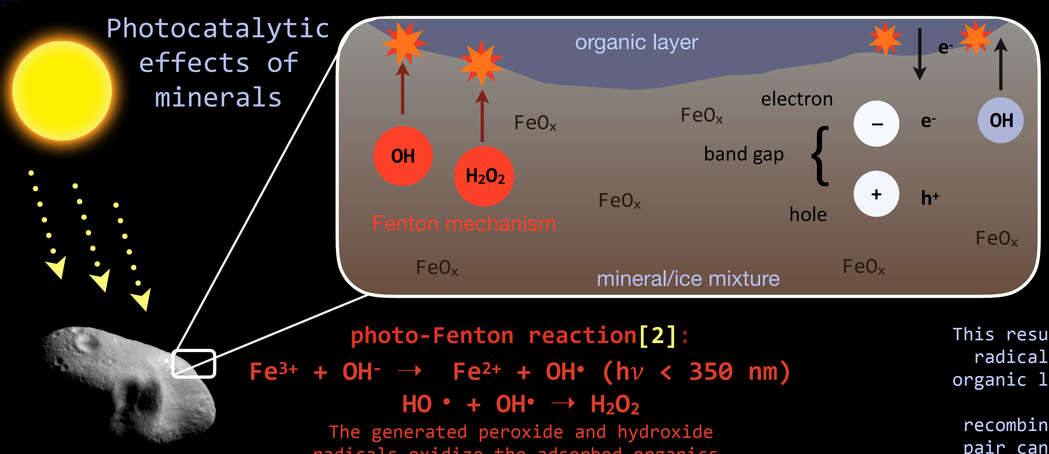


photo-Fenton reaction[2]:

$Fe^{3+} + OH^- \rightarrow Fe^{2+} + OH^\bullet$ ($h\nu < 350$ nm)

$HO^\bullet + OH^\bullet \rightarrow H_2O_2$

The generated peroxide and hydroxide radicals oxidize the adsorbed organics.

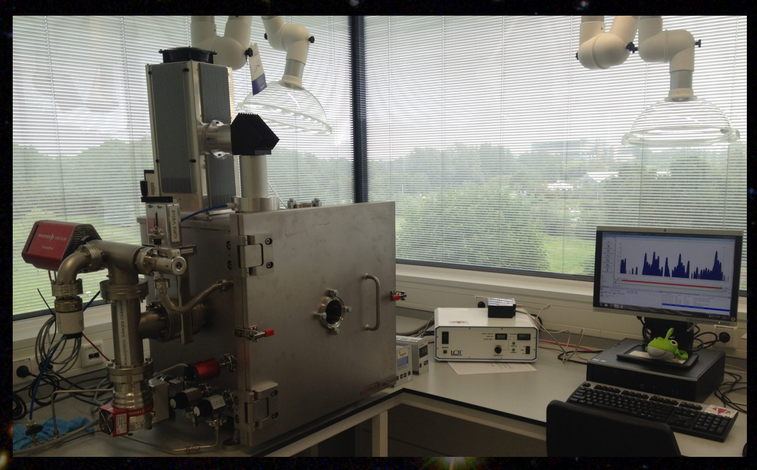
generation of electron-hole pairs:

Photoexcitation in semiconductors causes charge separation between the valence and conduction bands which yields trapped electrons (e^-) and electron deficiencies (h^+)[3].

This results in the formation of OH radicals which can react with the organic layer. Charge transfer from the organic layer for the recombination of the electron-hole pair can also directly oxidize it.

Laboratory Simulations

Planetary **A**nalogs **L**aboratory for **L**ight, **A**tmosphere, & **S**urface simulations [5]



Simulate the early Earth or Mars

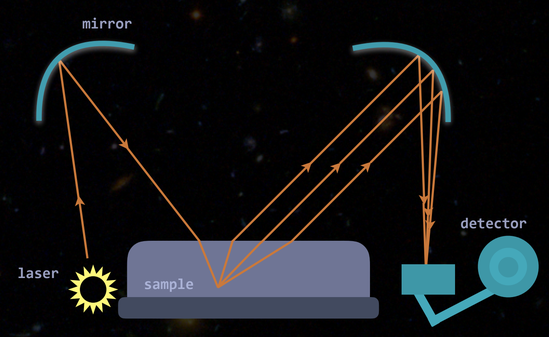
Solar UV radiation (190-900 nm)

Low temperature (-80 to +22 °C)

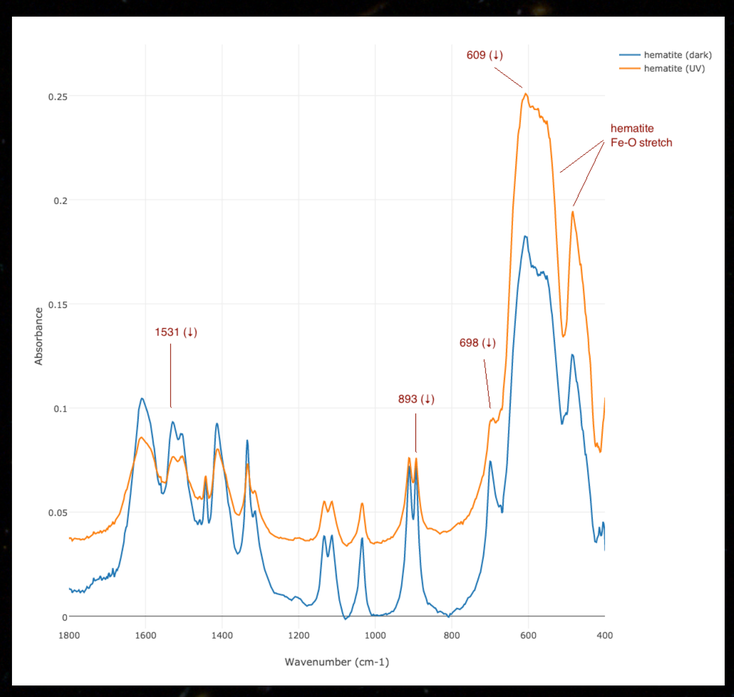
Custom atmosphere or vacuum (10^{-7} mbar)

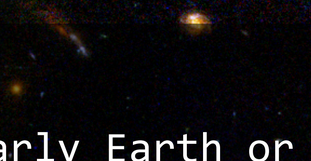
Analytical Techniques

Diffuse reflectance infrared spectroscopy (DRIFTS)



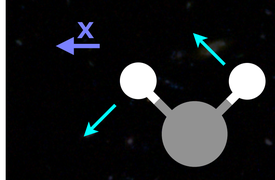
DRIFTS spectra of (non)irradiated glycine on a hematite substrate in PALLAS



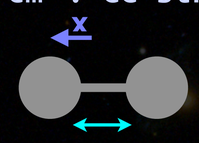


When glycine is oxidized, it gradually loses its functional groups, which manifests itself in the spectra as a decrease or shift in the peaks corresponding to the movement of those bonds.

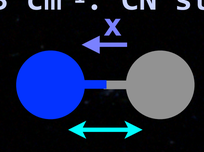
609 cm^{-1}: CH_2 rock [6]



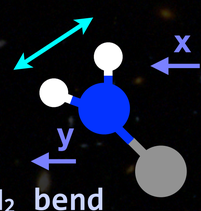
698 cm^{-1}: CC stretch



893 cm^{-1}: CN stretch



1531 cm^{-1}: NH_2 bend



References:

[1] Bob Downs (2017). RUFF Database, RRUFF.info.
[2] Fenton, H. J. H. (1894). *Journal of the Chemical Society, Transactions, 65,* 899-910.
[3] Shkrob, I. A., et al. (2010). *Astrobiology, 10*(4), 425-43.
[5] ten Kate, I.L., & Reuver, M. (2016). *Netherlands Journal of Geosciences, 95*(2): 183-189.
[6] Rosado et al. (1998). Vibrational Spectroscopy, 16(1), 35-54.