

Adsorption and surface complexation study of nucleotides on aluminum oxide surfaces

C. FEUILLIE^{1*}, D.A. SVERJENSKY² AND R.M. HAZEN¹

¹Geophysical Laboratory, Carnegie Institution, Washington D.C. 20015

(*correspondance : cfeuille@ciw.edu) (rhazen@ciw.edu)

²Dept. of Earth and Planetary Sciences, Johns Hopkins University, Baltimore M.D. 21218 (sver@jhu.edu)

In the context of the origin of Life, mineral surfaces might be important in the formation of the earliest biopolymers, such as nucleic acids, by trapping and concentrating their elementary bricks, as well as catalysing prebiotic reactions. The interaction of nucleotides with minerals has therefore been the focus of many studies, mainly regarding clay minerals [1] but also metal oxides such as rutile [2] or alumina [3].

Here we investigate the interactions between nucleotides, 5'-GMP, 5'-CMP, 5'-AMP and 5'-UMP, and α -alumina surfaces. We carried out batch adsorption experiments over a large range of pH, ionic strength and surface loading. Alumina adsorbs very high amounts of nucleotides $> 2 \mu\text{mol}/\text{m}^2$. We also performed surface complexation modeling in order to establish the speciation of the surface species, and the stoichiometry and the thermodynamic equilibrium constants for the adsorption of nucleotides on alumina surfaces. We used the extended triple-layer model (ETLM), that takes into account the electrical work linked to the desorption of chemisorbed water molecules during the formation of inner-sphere complexes. Results point to the formation of two surface species on the surface of corundum : a monodentate inner-sphere complex, and a bidentate outer-sphere complex, both involving interactions between the negatively charged phosphate group and the positively charged surface of alumina. This is in good agreement with previous computational results [4].

[1] Ferris (2005), *Reviews in mineralogy & geochemistry* 59, 187-210. [2] Cleaves, Jonsson C.M., Jonsson C.L., Sverjensky & Hazen (2010), *Astrobiology* 10, 311-323. [3] Arora & Kamaluddin (2009), *Astrobiology* 9, 165-171. [4] Fry, Kwon, Komarneni, Kubicki & Mueller (2006), *Langmuir* 22, 9281-9286

Sources and chemistry of nitrate in snow at Summit, Greenland

D.L. FIBIGER¹ M.G. HASTINGS² J.E. DIBB AND L.G. HUEY⁴

¹Brown University, Department of Chemistry, 324 Brook St., Providence, RI 02912, USA, dorothy_fibiger@brown.edu

²Brown University, Department of Geological Sciences/Environmental Change Initiative, Providence, RI, USA, meredith_hastings@brown.edu

³University of New Hampshire, Earth System Research Center, Insitute for the Study of the Earth, Ocean and Space, Durham, NH, USA, jack.dibb@unh.edu

⁴Georgia Institute of Technology, School of Earth and Atmospheric Sciences, Atlanta, GA, USA, (greg.huey@eas.gatech.edu)

Atmospheric nitrate deposition to snow surfaces results from reactions of NO_x (NO and NO_2) with oxidants, which produce HNO_3 that is taken up on the surface of particles or incorporated into precipitation. The concentration and isotopic composition of nitrate (NO_3^-) in ice cores have been studied with the aims of reconstructing past NO_x concentrations in the atmosphere, modeling past atmospheric oxidant concentrations and exploring variability in NO_x sources.

In a campaign consisting of two springtime (May-June) field seasons at Summit, Greenland [$72^\circ 35' \text{N}$, $38^\circ 25' \text{W}$], atmospheric and surface snow measurements were made to investigate NO_x sources contributing to the snow NO_3^- . Specifically, we look to use the nitrogen ($\delta^{15}\text{N}$) and oxygen isotopic composition of nitrate ($\delta^{18}\text{O}$, $\Delta^{17}\text{O}$) to track sources, chemistry and processing of the snow nitrate.

In surface snow collected several times each day during the springtime field seasons, $\Delta^{17}\text{O}-\text{NO}_3^-$ ranges from 5-35‰, $\delta^{18}\text{O}-\text{NO}_3^-$ from 35-85‰ vs. VSMOW, and $\delta^{15}\text{N}-\text{NO}_3^-$ from -7 to 13‰ vs. air N_2 . No relationship is found between the concentration of NO_3^- in snow and the isotopic composition of NO_3^- . A striking correlation between $\Delta^{17}\text{O}$ - and $\delta^{18}\text{O}-\text{NO}_3^-$ is found throughout both field seasons, with a slope of ~ 0.5 and $r^2 > 0.9$. This relationship appears to be a direct result of atmospheric production of NO_3^- , without significant post-depositional processing. Comparison of the $\delta^{15}\text{N}$ data with $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ suggest a three-point mixing between three NO_3^- sources with the following isotopic compositions ($\delta^{15}\text{N}$, $\Delta^{17}\text{O}$, $\delta^{18}\text{O}$ (‰)): (1) -8, 27, 74 (2) 6, 40, 100 and (3) 16, 0, 23. While the same three NO_x pools appear to be influencing the deposited nitrate in 2010 and 2011, there appears to be different relative contributions in the two different years. The $\delta^{15}\text{N}$ of NO_x sources has not been well quantified, but by combining nitrogen and oxygen isotopic data, we are able to assign tentative identities to the three sources.