Anions dramatically enhance proton transfer across the air-water interface

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Fundamental processes in chemistry and biology are driven by proton transfer (PT) across water interfaces with hydrophobic media. However, what distinguishes PT 'on water' from conventional PT 'in water' remains unclear. Here we show that PT from gaseous nitric acid to liquid water is dramatically accelerated by non-specific anions. We found that $HNO_{3(g)}$ fails to dissociate on pure water surfaces but is fully deprotonated on 1 mM electrolytes. Quantum mechanical (QM) calculations confirm that $HNO_{3(g)}$ dissociation on pure water is unfavorable and show that anions pre-organize interfacial water, thereby setting the stage for adiabatic PT. Our findings provide direct evidence of the critical role electrostatic pre-organization plays in catalyzing proton transfers across water-hydrophobe interfaces, such as those involved in cloud acidification and enzymatic events.

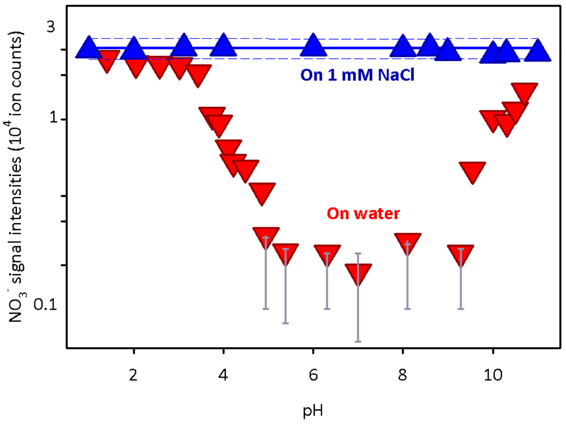

Figure 1: Electrospray ionization mass spectral nitrate (m/z = 62) signals detected on water or 1 mM NaCl microjets exposed to 0.4 ppbv gaseous nitric acid for ~ 10 μs as functions of water pH. Solid, dashed lines are a linear regression and its 95% confidence limits, respectively, to the data obtained on 1 mM NaCl. Error bars estimated from reproducibility tests. All experiments in 1 atm of $N_{2(g)}$ at 300 K.

George Tilton: Pioneer of lead isotope geochemistry

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George Tilton, who died on October 12, 2010, was one of the giants of isotope geochemistry and cosmochemistry. He is best known as the father of U-Pb dating of zircons and other minerals, a method for measuring ages of minerals and rocks that now yields uncertainties of one million years or less, for rocks and meteorites as old as 4.5 Ga. Thousands of papers have been published based on this method.

George Tilton also contributed pioneering work applying lead isotopes to measure the age of the solar system and to determine the evolution of the Earth. Later in his career, he turned his attention to the isotope geochemistry of carbonatites.

I will highlight some of George's landmark contributions and discuss the current state of some of the enduring puzzles, often called "paradox", posed by the lead isotope systematics of modern and ancient rocks. I will also discuss two basic questions that continue to engage isotope geochemists: (1) Did the U/Pb ratio of the accessible silicate Earth increase subsequent to accretion and core formation, and if so, why? (2) Why did the Th/U ratio of the accessible Earth begin with an apparently superchondritic value in Hadean time and decrease to subchondritic values subsequently? Answers to these seemingly arcane questions are fundamental to understanding the origin and global evolution of our planet.