DRY ACID DEPOSITION AND ACCUMULATION ON THE SURFACE OF MARS AND IN THE ATACAMA DESERT, CHILE. R. C. Quinn[1,3], A. P. Zent[2], P. Ehrenfruend[3], C. L. Taylor[1], C. P. McKay[2], J.R.C. Garry[3], F. J. Grunthaner[4], [1]SETI Institute, NASA Ames Research Center, MS 239-12, Moffett Field, CA 94035 (rquinn@mail.arc.nasa.gov), [2]NASA Ames Research Center, Moffett Field, CA 94035, [3]Leiden Institute of Chemistry, Leiden University NL, [4]NASA Jet Propulsion Laboratory, Pasadena, CA 91109.

Introduction: It has been discovered recently that soils from certain regions of the Chilean Atacama Desert have some characteristics that are similar to the surface materials tested by the Viking Landers. Navarro-González et al.[1] demonstrated that the quantity and diversity of heterotrophic bacteria increase as a function of local water availability in the Atacama, and that for some soil samples collected in the driest regions, no culturable bacteria could be isolated. Additionally, Navarro-González et al. reported that pyrolysis-GCMS analysis of soils collected from these regions revealed extremely low levels of organic matter. Although the mechanism resulting in the low level of organics in these regions was not established by Navarro-González, the condition of organic-depleted, near-sterile soil offers an interesting Earth analog of the martian surface material, as the Viking Gas Exchange (GEx) experiment and Labeled Release (LR) experiment were unable to demonstrate the presence of culturable bacteria [2], and the Viking pyrolysis-GCMS was unable to detect organic compounds [3].

We have examined the acid-base equilibration kinetics of soils collected in the Chilean Atacama Desert and compare these results to information on the acid-base chemistry of martian surface samples derived from the Viking experiments. Soil pH is of interest because it plays a direct role in a number of processes that affect soil mineralogy, organic chemistry and soil biological load. The recent discovery at the Mars Exploration Rover (MER) Opportunity site of jarosite [4], which forms in strongly acidic-sulfate rich environments, heightens the importance of understanding the chemical state of the martian surface material and its behavior in aqueous systems. Some experimental information on the chemical behavior of the martian surface in aqueous systems can be deduced from the Viking biology experiments. These biology experiments revealed that multiple chemical reactants were present in the surface material and that a minimum of three oxidizing species are needed to explain the experimental results of both the GEx and LR [2]. Although examined less than the data that indicates that the martian surface material is oxidizing, the first information on the acid-base chemistry of the surface material was also returned by the Viking biology experiments. Viking did not measure pH directly, but examination of CO_2 partitioning between the head-space and aqueous phases in the biology experiments can yield insight into the acid-base chemistry of the surface material at the landing sites.

Results and Discussion: We have measured the pH of soil samples collected along a north-south transect (24°S to 28°S; ~ 70°W) in the Chilean Atacama Desert and compared the magnitude and kinetics of pH shifts in these soils upon wetting with pH changes occurring in Viking martian surface samples wetted in the Labeled Release experiment. We have estimated the pH changes occurring when the Viking 1 LR cycle 2 experiment surface sample was wetted by converting the quantity of CO_2 adsorbed or desorbed due to pH shifts to equivalent H^+ using carbon dioxide/carbonic acid equilibrium calculations. When experimentally wetted, the pH of both the Viking and surface sample collected from the dry core of the Atacama Desert (Yungay) surface samples underwent a rapid shift, similar in magnitude, from acidic to slightly basic. This shift was not observed in samples collected from wetter regions of the Atacama or from the subsurface at Yungay (figure 1). The pH response of surface soils collected at the Yungay site is consistent with the dry deposition and accumulation of atmospheric acid aerosols and acid precursors on the soil surface at the Yungay site. The absence of this acid component in the subsurface samples is consistent with a water transport mechanism for soil horizon formation in thedesert. It appears that the low moisture levels in

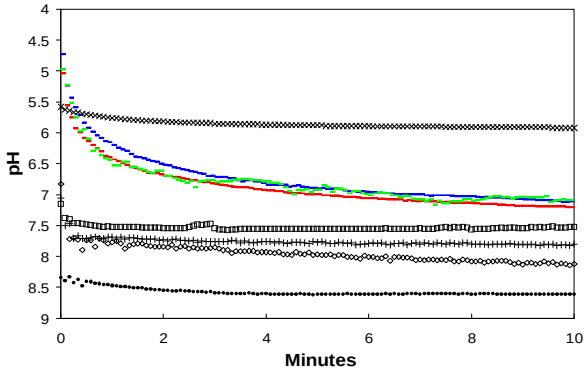

Figure 1. The pH response of Atacama surface soils (collected along a north–south transect, @ ~ 70°W) when wetted. -·- Yungay surface samples 24° 4' 10"S; ◊ 24° 34' 26"S; x 25° 4' 6"S; □ 25° 18' 17"S; + 25° 45' 37"S; * 28° 7' 5"S.

Yungay result in acids accumulating at the surface; accumulation continues until offset by the periodic addition of sufficient amounts of water (either through rain or fog) to cause dissolution and neutralization.

In figure 2 the response of the VL1 LR cycle 2 sample is plotted as moles of aqueous H^+ in the soil solution as a function of time, overlaid with a pH data for Yungay surface samples (also reported as moles of aqueous H^+ in the soil solution). The total moles of aqueous H^+ in the Atacama soil solution was normalized to the 0.5 cc Viking LR sample volume. The number of moles of H^+ released into solution by the Yungay soil is comparable to the amount released by the VL1 cycle 2 sample. The measured kinetics, however, are different. These differences can be explained by the different experimental techniques used to derive the H^+ changes. Based on the data derivable from Viking, the response of the Yungay samples upon wetting is consistent with the LR observations and can be explained by the rapid solvation of a soil acid followed by neutralization.

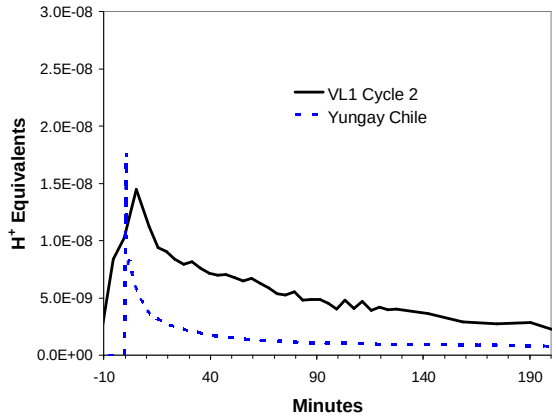

Figure 2. Response of the VL1 cycle 2 labeled release sample and Yungay surface sample shown as H^+ equivalents.

Using the Mars Oxidation Instrument (MOI), we have further characterized the acidic Yungay surface environment. MOI is chemiresistor-based sensor array that measures the oxidation rate of chemical films that are sensitive to particular types of oxidants or that emulate prebiotic materials. With these sensors the chemical reactivity of a planetary environment is characterized by monitoring the resistance of the film as a function of time. The sensors were deployed in the field to discriminate the effects of UV and dust from soil reactions. One set of sensors was exposed to dust, direct UV, and the atmosphere; another set was shielded from direct UV and dust exposure; and the third set of sensors was deployed face down in the soil, blocking UV radiation, dust accumulation, and direct atmospheric exposure. By monitoring differences in film reactions among the electrodes, this deployment mode measures the relative contributions of soil chemistry, UV photochemistry, and dust/aerosol chemistry to environmental oxidation processes. Representative responses of the MOI sensors are shown in figure 3. The sensor responses are consistent with an oxidative attack by strong acids triggered by dust accumulation followed by transient wetting due to an increase in relative humidity during the night. We conclude that in the Atacama Desert and on Mars, extremely low pH resulting from acid accumulation, combined with limited water availability and high oxidation potential, will result in acid-mediated reactions at the soil surface during low- moisture transient wetting events (i.e. thin films of water). These soil acids are expected to play a significant role in the oxidizing nature of the soils, the formation of mineral surface coatings, and the chemical modification of organics in the surface material.

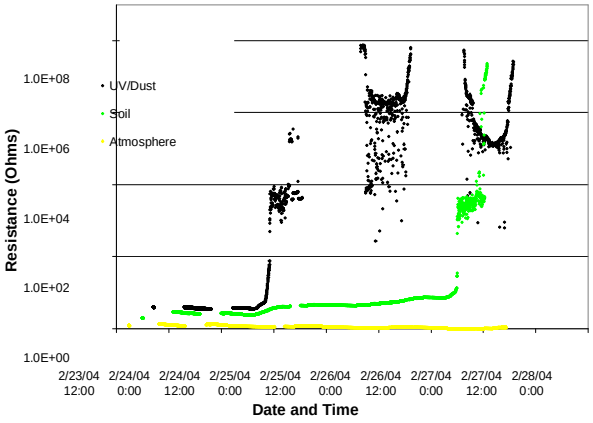

Figure 3. Sample results from the MOI Atacama field tests. Distinct reaction patterns are observed for each of three different sensor deployment modes. Reactivity was highest and reaction kinetics were fastest for sensors exposed to atmospheric dust. For the UV/Dust sensors, reaction proceeded after a twenty four hour dust accumulation period followed by an increase in atmospheric humidity at night. Atmospheric sensors shield from dust did not exhibit this response. Sensors exposed to soil displayed slower reaction kinetics due to buffering of humidity by the soil.

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References: [1]Navarro-González, R. et al. (2003) Science, 302, 1018-1021. [2]Klein, H. P. (1979) Rev. Geophys. Space Phys., 17, 1655-1662. [3]Biemann, K., and Lavoie, J.M. (1979) J. Geophys. Res., 84, 8385-8390. [4] Squyers, S.W. et al. (2004) Science, 306, 1709-1714.