A RUGGED MINIATURE MASS-SPECTROMETER FOR MEASURING AQUEOUS GEOCHEMISTRY ON MARS. L. C. French[1], F. S. Anderson[1], G. McMurtry[1], E. Pilger[1], J. Stopar[1], [1]University of Hawai'i at Manoa, Hawai'i Institute of Geophysics and Planetology, 1680 East-West Road, POST 526B, Honolulu, HI 96822 (french@higp.hawaii.edu, anderson@higp.hawaii.edu)

Introduction: We are developing a miniature, shock-hardened rotating field mass spectrometer (RFMS) for high precision measurements of aqueous geochemistry on Mars under MIDP funding. The design is based on a mass spectrometer system currently being used in-situ in deep ocean applications [1] and in the defense industry. The strengths of this instrument include: the ability to sample liquids, small dimensions, low power requirements, low mass, no precision machining is required, and it is tolerant of moderate vacuum.

The discovery of extensive near-surface deposits of ice in the northern lowlands of Mars [2,3] immediately raises the question of the nature and origin of these deposits. This new discovery of extant water raises the possibility of in situ studies of evaporite deposits in the process of formation, with water (almost certainly in the form of ice) within the reach of rover arms, shallow drills, or moles. An important question regarding the northern lowlands water ice deposits is their origin: are they the remains of a relic ocean, derived from discharge from the highlands into the lowlands? Or are they atmospheric condensates with only limited opportunity to leach ions from solids in contact? A potential means of distinguishing between these hypotheses is the nature and content of dissolved ions in the water. For example, the distribution coefficients of many ions are surprisingly large, *e.g.* on the order of 0.1 to 0.3 for only modest salinities [4,5]. Thus a frozen ocean or groundwater deposit, with extensive opportunity to leach ions from susceptible silicates when in the liquid form, will certainly have a much higher content of dissolved ions than a condensate, as well as likely showing a distinctive isotopic signature having been at least partly shielded from extensive atmospheric isotopic processing. Mass spectroscopy is an attractive experimental methodology for aqueous geochemical analysis. Expected species are distinct in mass/charge, and mass spectroscopy is sensitive to small (ppb) amounts of ions or dissolved gases.

Background: The presence of water on Mars is well established. A fundamental and unknown property of water on Mars is its geochemistry: what dissolved ions are present and what are their concentrations? Water in the liquid phase will interact with solid material thus dissolving and mobilizing soluble species. During freeze-thaw cycles, liquid water can react with the solids, changing the water's composition. This happens at low temperature and preferentially involves the smallest grains, which will likely lead to a new ionic composition being reflected in the refrozen ice. An intriguing possibility is thin films of water might be present, about soil grains, and if we could sample them before measuring the composition of the main mass of ice, we might be able to determine their presence, composition, and effect on the overall ice composition. At the other extreme, hydrothermal circulation likely will result in water with increased levels of dissolved ions. If hydrothermal waters flowed onto or near the surface, they would likely freeze, leading to zoned deposits of ice and, with evaporation, zoned mineral deposits [6].

[4] found that solutes are concentrated in liquid water with a distribution coefficient (the ratio of the concentration in the solid to the liquid) of 0.3 in freezing columns of brine-saturated sand. It is clear that as water freezes on Mars it includes significant amounts of solute. Although these effects can be reduced by thaw-freeze cycles (as has been observed in sea ice), it can also be argued that they can enhance fractionation, hence a detectable remnant signature is likely. The project will build an instrument that can directly analyze water that will have mobilized leached ions and that is accessible with modest mission sampling methodologies.

Method: The RFMS uses "rotating" RF electric fields and was invented by Co-investigator Smith [7]. It consists of an ionizer, a mass spectrometer and an ion detector (**Fig. 1**). The sample flow output is introduced into a liquid nanospray ionization stage. The resulting sampled ions are focused into a beam (500-600 eV energy with 1 eV energy width) that enters a cell-like region with sinusoidal RF fields in the x- and y- direction that differ in phase by 90 degrees. The ions of a particular mass travel in a helix and impact an ion detector at the end of the cell. The ions generate a pattern which appears as a set of concentric circles, much like the lissajou figures generated by a dual channel oscilloscope driven at the same frequency but with the channels differing by a 90 degree phase angle. The choice of RF frequency and amplitude determines the particular ion mass to be selected.

The normal electrospray is adapted by two important changes. First, the ESI is directly admitted into the vacuum chamber. Second, an "anode cap" covers the spray nozzle, which is a pinhole aperture held at the desired electric potential of the beam. This aids greatly in defining the precise energy of the "beam" of ions that are produced.

The existing ESI-RFMS has produced a range of spectra for a variety of materials with better than 1 part in 1000 mass resolution. The RFMS has measured ar-

gon and large organic compounds (C_6F_{12}, mass 300 amu), lysozyme with mass greater than 14,000 Dalton (**Fig. 2**), as well as adenosine, angiotensin, and seawater liquid samples where various mineral solutes are seen clearly. However, there remain issues associated with reproducibly generating stable electrospray and instrument SNR. Under MIDP, we have focused on creating reproducible electrospray on demand, by building a new generation of in vacuum electrospray ionization sources (**Fig. 3**).

Results: Figure 4 shows the ion current as a function of pressure, with color indicating the applied voltage. Data collected when no voltage was applied have been removed. The ion current produced is relatively stable at each applied voltage, though less stability is observed at the highest and lowest pressures in each cycle. One can clearly see the dual ion current regimes under an applied voltage of 100 V. At low pressures, a high ion current (~150 pA) was produced, while at high pressures the current was limited to ~10 pA. This may indicate that the ions had insufficient energy to penetrate the atmosphere in the chamber at pressures ~> 2 Torr. Despite significant pressure variations, the ion current does not vary significantly. Most of the data was collected during the cyclical pressure variations generated by the spray of 1.3 to 2.7 Torr. The 800 V data, shown in yellow, dips below a pressure < 1.3 Torr during a period when no ethanol was provided to the electrospray head, and the pressure fell as the highly volatile ethanol was replaced by non-conductive air. This can also be seen as a gentle yellow arc of data leading from the main yellow cloud down to the values < 1.3 Torr.

We have improved these initial results by completely stabilizing the electrospray by increasing the surface tension of the spray with water, and directly electrifying the ESI interface, producing 10^4 more ions, and dramatically increasing our SNR over the results shown here. We believe that this MIDP work has paved the way for the use of ESI in vacuum, reducing the mass required for a flight instrument dramatically.

References:

[1] McMurtry, G. M. and S. J. Smith, Proceed. Oceans 2001, Marine Tech. Soc. and IEEE, Honolulu, 259-263. [2] Boynton, et al, *Science*, 297, 2002. [3] Feldman, et al, *Science*, 297, 2002. [4] Baker, G. C. and Osterkamp, T. E. (1999), *Water Resour. Res.* **25**, 1825–1831. [5] Nakawo, M. and Sinha, N. K. (1981) *J. Glaciol.* **27(96)**, 15-330. [6] Catling, D.C. (1999), *Journal of Geophysical Research,* **104**, 16,453-16,469. [7] Smith, S. J. and A. Chutjian, , *NASA Tech. Briefs*, February, 1998.

Figure 1. RFMS mass filter and detector subsystem (< 4" long).

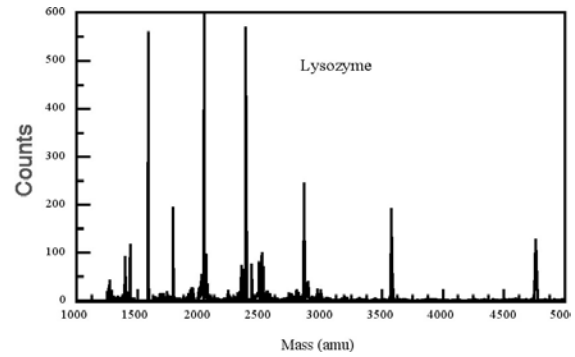

Fig. 2. Multiple charging of organic Lysozyme spectrum.

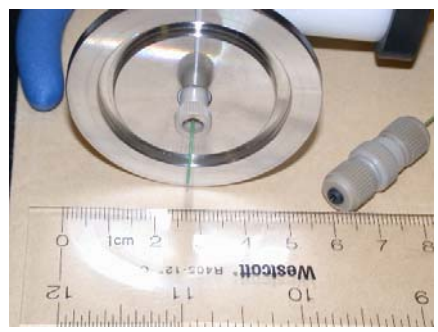

Figure 2. 100 micron electrospray needle, KF40 vacuum flange, and sample filtration/uptake system (right). Tips can be easily changed to a different size or type or replaced entirely in a matter of minutes.

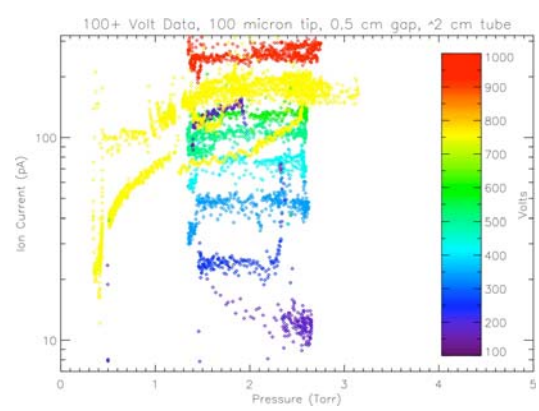

Figure 3. Ion current versus injection voltage shows relatively stable ion production, despite significant variations in pressure. We have now stabilized pressure, and increased the ion signal by 4 orders of magnitude using direct electrification of the ESI needle. This bodes well for stable and reproducible mass spectroscopy.