ANALYSIS OF SYNTHETIC TERRESTRIAL AND MODELED ENCELADIAN SEAWATER USING THE MICROFLUID WET CHEMISTRY LABORATORY (mWCL).

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Introduction: The 2008 Phoenix lander mission provided the first successful soil analysis of the Martian surface. Utilizing the on board Wet Chemistry Laboratory (WCL) revealing the chemical composition and potential habitability of the planet. This was achieved by a simple array of ion selective electrodes (ISEs) which analyzed the geochemistry of the Martian soil providing invaluable information into not only the aqueous geochemistry but the history of Mars [1,2].

As such, similar technology can be utilized to assess the ocean composition of icy moons, such as Europa and Enceladus. A redesigned TRL9 Phoenix WCL array with microfluidic platform will allow analysis of either ejected plumes or liquid brine from the moons subsurface oceans. These analyses will provide essential data about the chemical energy, redox gradients, subglacial ocean geochemistry as well as the habitability of these icy ocean worlds

Prior to using the Phoenix heritage sensors for icy worlds analysis, the manifold was restructured to house a full array of ISEs, conductivity sensor, to operate with material from ejected plumes or collected from the surface; to function with microliters of sample and be durable to withstand the extremes and zero g encountered on a ~10 year cruise in deep space. Previous work assessed the mWCL ISE's sensitivity, stability, and showed that they are long lasting, robust and comparable to the phoenix heritage ISEs [3,4].

Current work has been aimed at evaluating the ISE's performance in the manifold (Fig.1), as well as in simulated ocean chemistries of Earth and Enceladus. These ISEs will determine both soluble anionic and cationic species and will therefore reveal the complex interactions between rock and water of the icy moons.

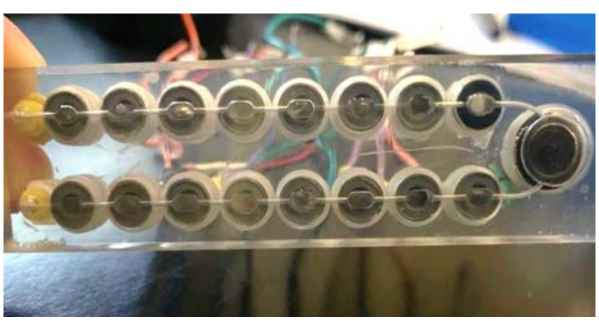

Figure 1. *Printed flow-through mWCL manifold containing 16 ISE sensors and a conductivity electrode.*

Methods: In this work, the ISE sensors were calibrated using standard solutions ranging in ionic concentration from 10^{-5} to 10^{-1} M (designated as CS10-14) and then used to determine concentrations of soluble inorganic ionic species and solution parameters. Synthetic terrestrial and modeled Enceladian seawater samples were created using estimated concentrations found in literature [5, 6].

The seawater samples were then used with the flow-through mWCL sensor array and with standalone sensors in a beaker, to study the effects of the high concentrations of ions expected on Enceladus and Europa that included sensors for (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- HSO_3^-, and $CO_3^=$.

Results: A study was initially performed to compare the response of the heritage ISE sensors used in the Phoenix WCL [1] to as used in the mWCL.

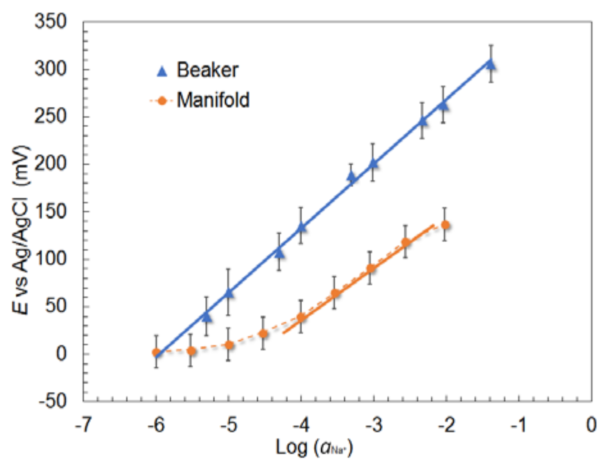

Figure 2. *Normalized response of ISE potential (E) vs Na^+ activity of eight Na^+ ISE sensors in the mWCL flow-through manifold compared to the same sensors tested in a beaker.*

Figure 2 shows, as an example, the average response of eight sodium (Na^+) ISE sensors in the mWCL flow-through manifold compared to the same sensors in a beaker. The largely unchanged heritage WCL sensors performed overall better in the mWCL array manifold than in the beaker, most likely due to the consistent and controllable laminar flow.

The mWCL Na^+ sensors responded linearly between an activity of 10^{-6} to 10^{-1} M with a slope of 68 mV/decade and a limit of detection (LOD) of 10^{-6} M. The sensors in the beaker on the other hand responded linearly only between 10^{-4} to 10^{-1} M with slope of 53 mV/decade.

To characterize the response of the mWCL sensor array to the ion concentrations expected to be present in the subglacial oceans of Enceladus, the sensors were calibrated with the CS10-14 standards in background solutions containing ion concentrations of either synthetic terrestrial seawater[5] or modeled Enceladian seawater [6].

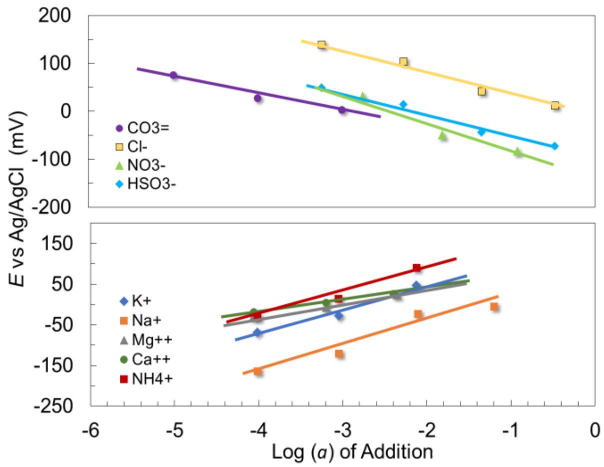

Figure 3. *ISE sensors in manifold tested by adding CS solutions 10-14 to synthetic terrestrial seawater.*

Figure 3 shows the linear response portion of the calibration curves for the ISE sensor array when the CS10-14 standard solutions with a synthetic terrestrial background were sequentially injected into the mWCL. Most of the sensors showed Nernstian behavior with slopes for some ions being slightly super- or sub-Nernstian but only by a 2-3 mV.

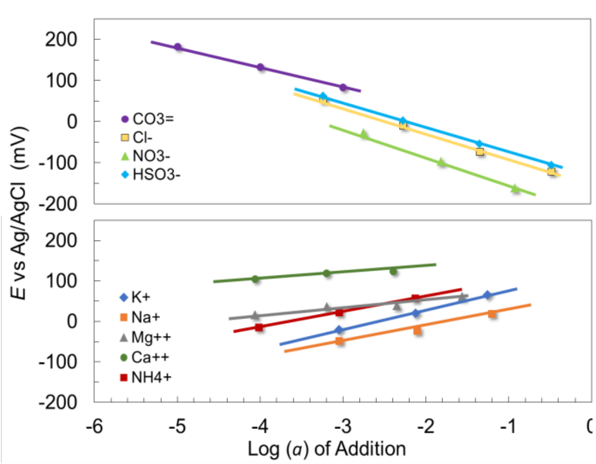

Figure 4. *ISE sensors in manifold tested by adding CS solutions 10-14 to modeled enceladian seawater.*

The same procedure as above for the terrestrial sample was used for the modeled enceladian seawater sample. Figure 4 shows the linear response portion of the calibration curves for the ISE sensor array when the CS10-14 standard calibration solutions were sequentially injected into the mWCL.

As expected, the higher concentration of Na^+, Cl^-, and $CO_3^=$, in the model enceladian seawater resulted in a substantial non-Nernstian response for several of the ISE sensors. All of the cation sensors (Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}) gave a ~20% sub-Nernstian slope. The responses for anion sensors were mixed, with the slope for the NO_3^- sensor being sub-Nernstian while that for the $CO_3^=$ sensor was super-Nernstian.

For both the terrestrial and Enceladian samples the sensors had limits of detection substantially higher than in the simple calibration solutions or when in the beaker. In all cases the LOD started to appear at around the 10^{-4} or 10^{-5} M concentration of the measured species, most likely due to the high ionic concentration of Na^+ and Cl^- in the samples.

To gain a better understanding of the ISE sensor behavior in the high concentration seawater sample, selectivity coefficients were determined for all the sensors in the mWCL array using the fixed interference method (FIM) and the matched potential method (MPM). With these values and the Nikolsky-Eisenman equation, we are further investigating the chemical and chemometric processes that would enable the mWCL to accurately measure the activities of soluble species in the presence of the interferants expected in enceladian seawater.

By determining the ionic composition and critical physical parameters of the captured frozen plume ice particles at Enceladus' or from surface samples on Europa, the mWCL will provide the information to determine the potential habitability of the subglacial oceans of these icy worlds.

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References: [1] Kounaves, S. P., et al. (2010) *JGR, 115*, E00E10. [2] Kounaves, S. P., et al. (2010) *GRL, 37*, L09201. [3] Oberlin, E. A., et al. (2017) *Astrobiology Science Conference*, Abstract # 3251. [4] Oberlin, E. A., et al. (2018) *NASA Exploration Science Forum*, Abstract #NESF2018-094. [5] ASTM International. *D1141-98(2013) Standard Practice for Preparation of Substitute Ocean Water*. [6] Zolotov, M. Y. (2007) *GRL, 34*, L23203