ION SELECTIVE ELECTRODES FOR SOLUBLE SALT MEASUREMENTS ON ICY WORLDS

A. C. Noell, E. A. Oberlin, A. M. Fisher, R. C. Quinn, A. J. Ricco, R. E. Gold and S. P. Kounaves

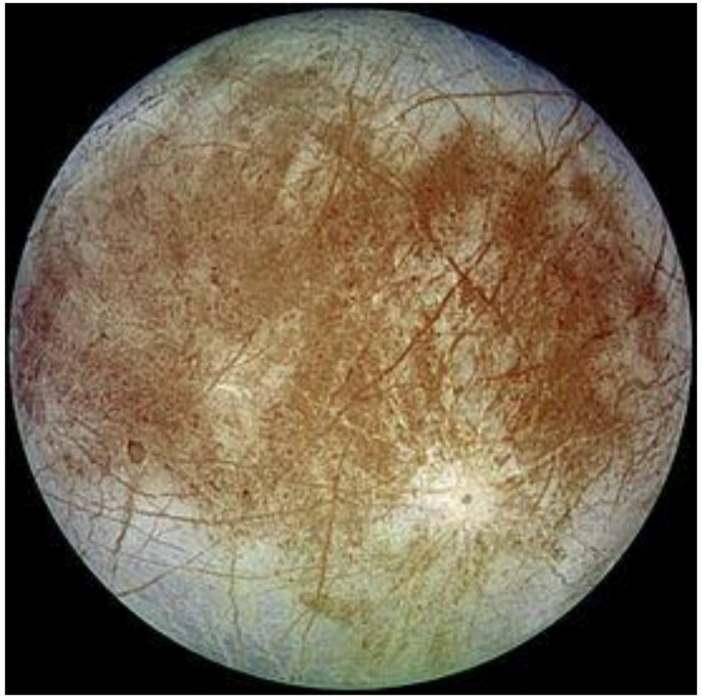
Jet Propulsion Laboratory, California Institute of Technology

Pasadena, CA (anoell@jpl.nasa.gov)

6/13/2018

Icy worlds are interesting because of their water and the life that might be at home in that water

- **Europa**
- SO_2
- H_2O_2
- H_2SO_4
- MgSO4
- NaCl



Europa. Credit NASA/JPL

- **Enceladus**
- NaCl
- $NaHCO_3$
- Na_2CO_3
- SiO_2

Plumes from Enceladus. Credit NASA/JPL

But it is the other things present in the water that will control whether life can survive and whether we can detect it!

Soluble species control the habitability of icy worlds

- **Hydrogen ion concentration (H_3O^+) or pH:** Life on Earth can survive over a wide range of pH's, but the specific pH of the system will dictates what chemistries are accessible to a microorganism

- **Chemical energy sources via the presence of Reduced and Oxidized (Redox) species:**

Example Metabolism name	Reduced species (Electron donor)	Oxidized species (Electron acceptor)
Anoxic ammonium oxidation	Ammonium (NH_4^+)	Nitrite (NO_2^-)
Iron oxidation	Ferrous Iron (Fe^{2+})	O_2, Nitrate (NO_3^-), Perchlorate (ClO_4^-)
Iron and sulfate reduction	Organics	Ferric Iron (Fe^{3+}), Sulfate (SO_4^{2-})
Nitrate and Perchlorate reduction	Organics	Nitrate (NO_3^-), Perchlorate (ClO_4^-)

- **Accessible sources of the major elements CHNOPS:** Molecules like Nitrate, Phosphate, and sulfate provide access to biologically useful Nitrogen, Phosphorous, and Sulfur

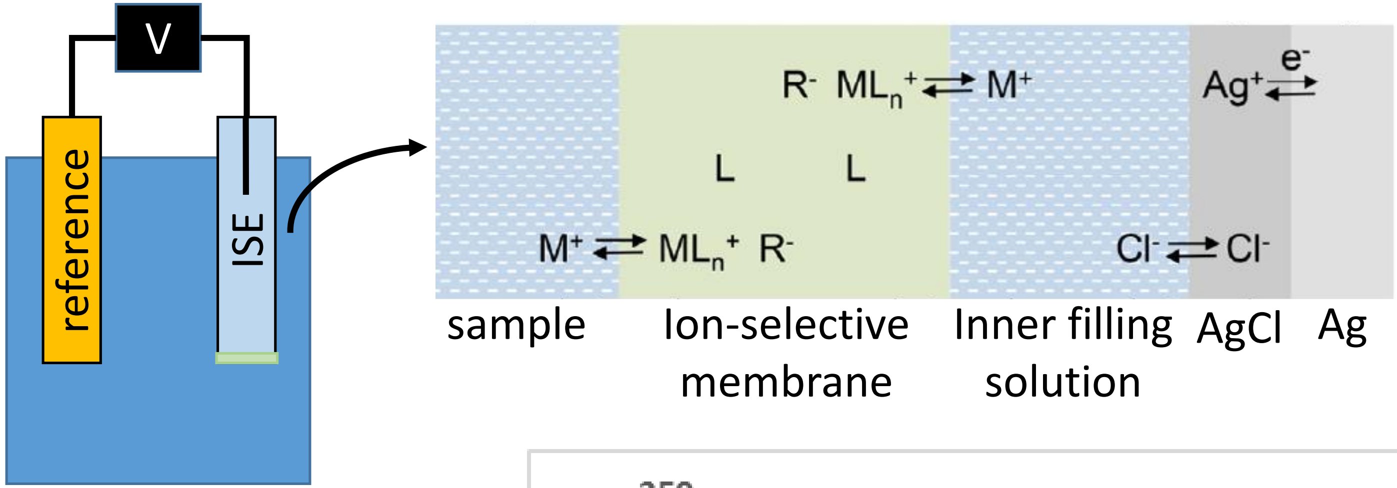
- **Bio-functional species and trace elements:** Ions are critical in biology for osmotic pressure (Na^+, K^+, Cl^-), Signaling (Ca^{2+}, Na^+, K^+), Enzyme function (Fe^{2+}/Fe^{3+}, Cu^{2+}/Cu^{3+}, Mn^{2+}/Mn^{3+} etc.), Protein folding (K^+, Mg^{2+}), Energy storage (PO_4^{3-})

Soluble species can provide sample context or interfere with measurements

- **Constraints on the sample age or the preservation potential of the sample matrix:** The presence of strong oxidants (ClO^-, H_2O_2) and the pH can help assess the age of the overall sample (oxidant concentration can be related to total radiation dose), as well as in what state biomolecules are likely to be found
- **Sample to sample heterogeneity vs. homogeneity:** The bulk properties of the samples can be monitored, if these change significantly then the sample may be changing from a bulk ice to a brine or an area with different history and processing.
- **Potentially interfering salts and ions:** Salts can interfere with derivitization schemes for volatilization or fluorescent tagging

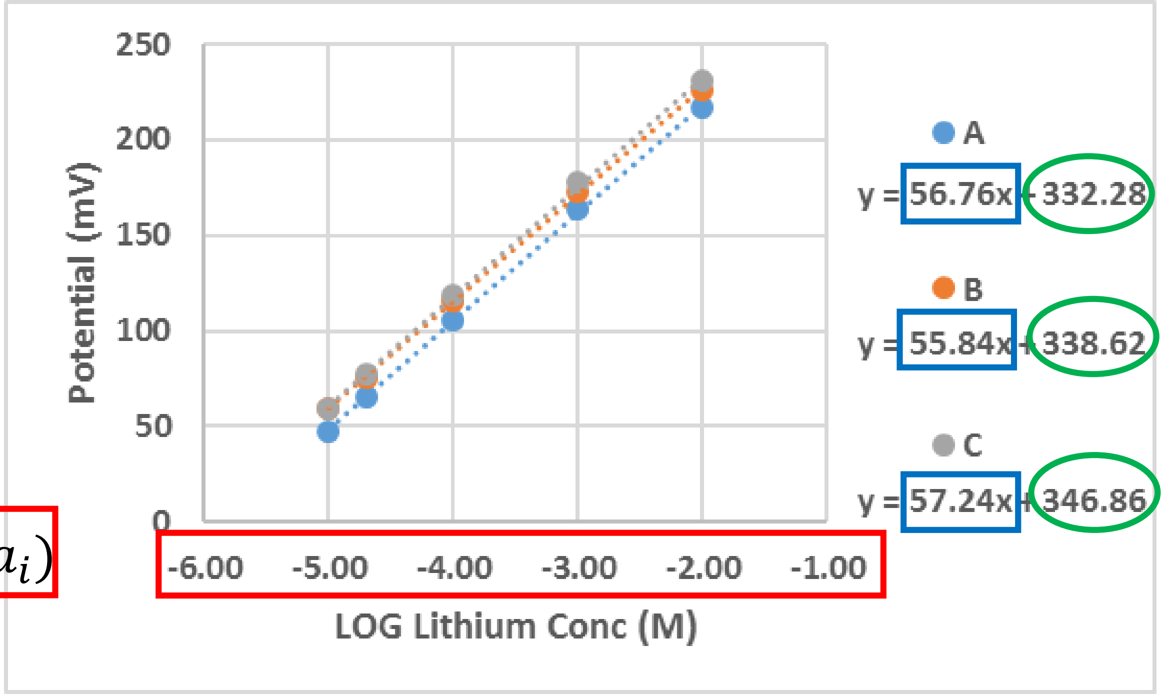
Ion selective electrodes (ISEs) measure soluble ions in samples

- ISEs are potentiometric measurements, no current flows
- The membrane potential responds to the selectively targeted ion and is the only changing potential
- Nernst equation leads to a fixed potential change per order of magnitude change in activity (concentration). Drift in E^0 requires calibration

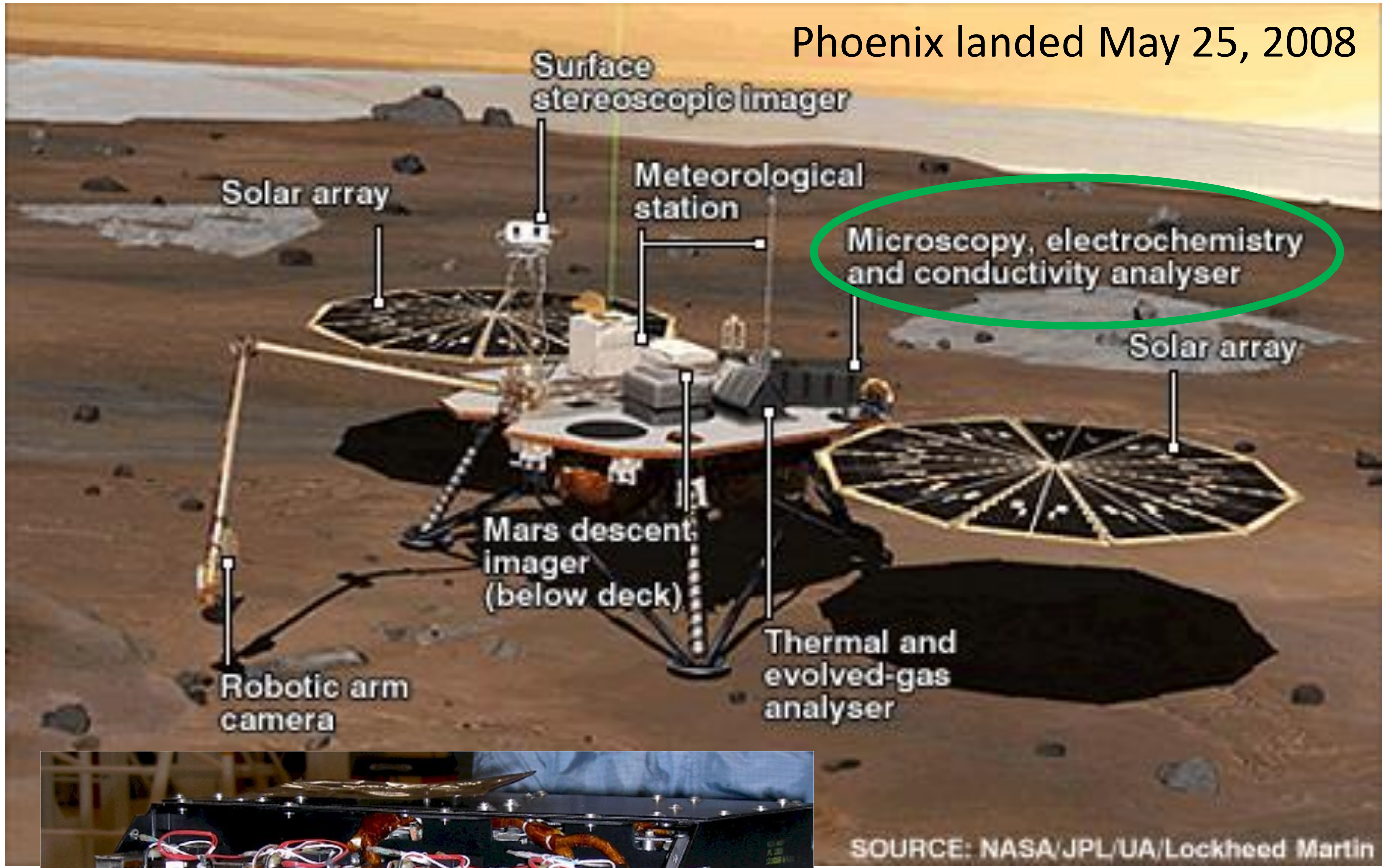


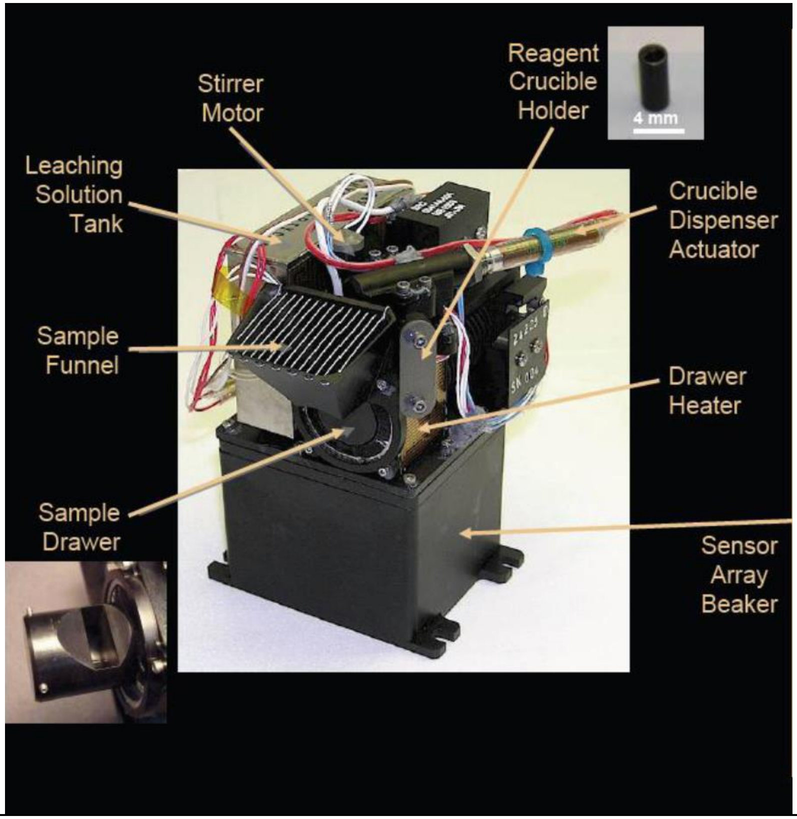
57 mV
1+ cations
At 25°C
↓

$$E = E_i^0 + \left(\frac{2.303RT}{z_i F}\right)\log(a_i)$$



ISEs successfully operated on Mars during the Phoenix mission



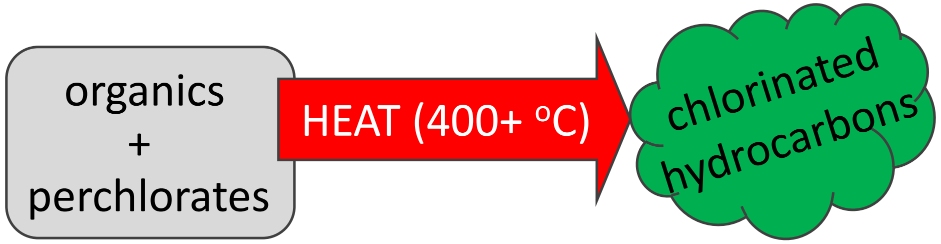


- **Measure Soluble Anions & Cations (ISEs)**
- **Measure pH (ISEs)**
- Measure Redox Potential
- Perform Cyclic Voltammetry
- Measure Conductivity
- Measure Oxidants

WCL measurements of perchlorate during the Phoenix mission as a case study on the importance of sample context

- ISEs as part of WCL made the unexpected discovery of significant amounts (0.6% wt) of perchlorate (ClO_4^-) in the Martian regolith
- This discovery helped explain observations made by both the Viking landers and Curiosity

Problem: Non-volatile species need substantial heating to vaporize, but…



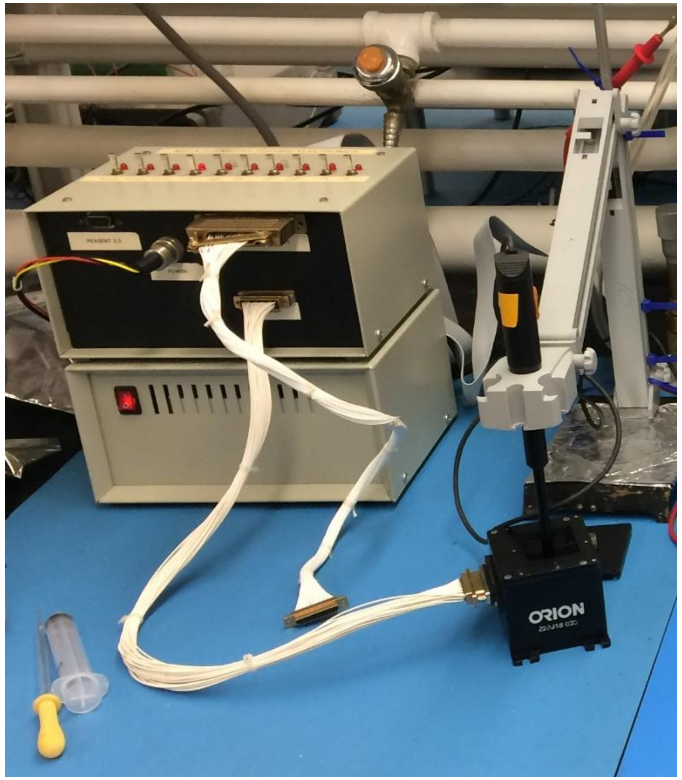
Chloro and dichloromethane (Viking, Curiosity)
Benzyl chloride (Curiosity)

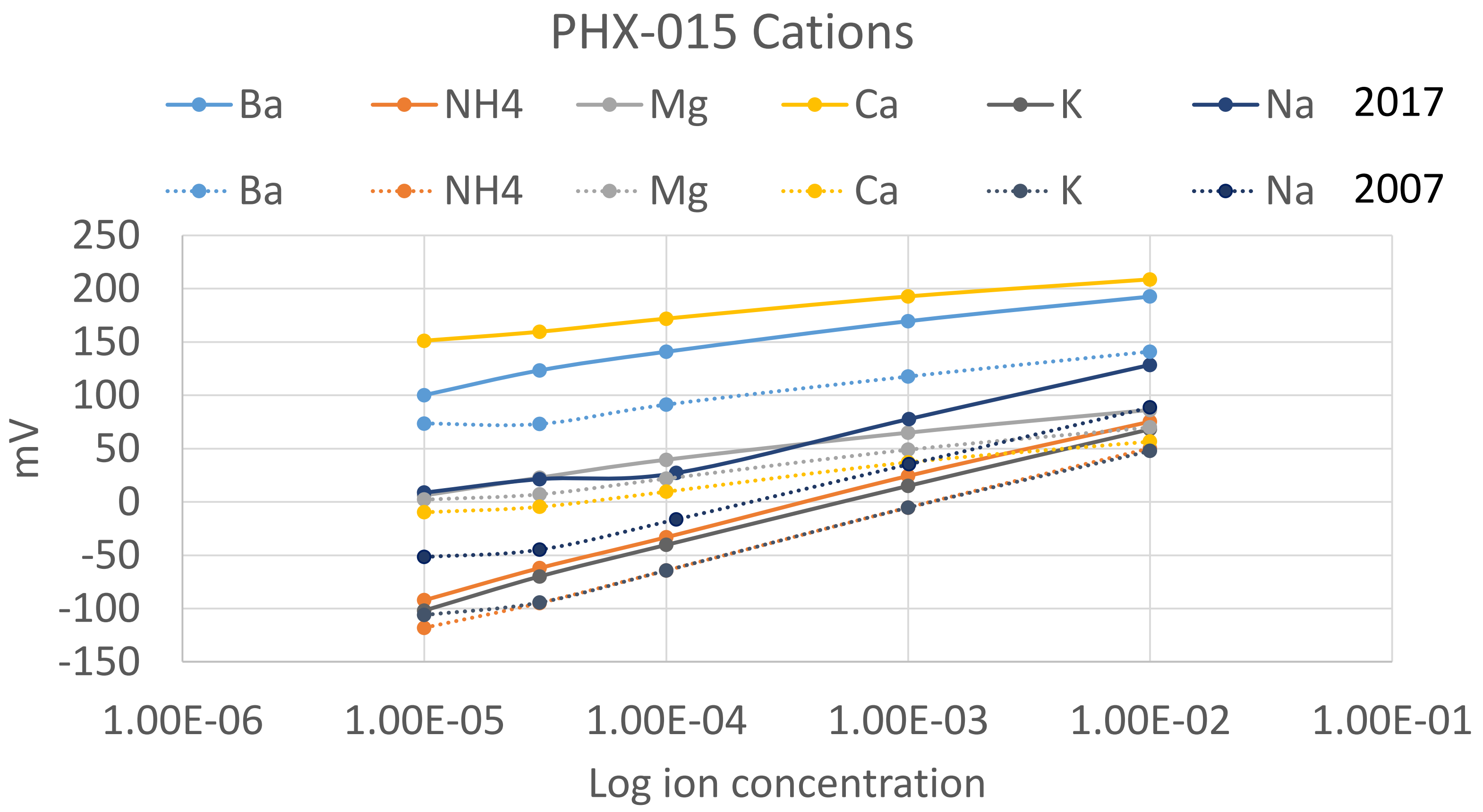
- The presence of ClO_4^- can also be used as an indicator of recent water flow as its high solubility means that it will be removed from anywhere where water has recently been in contact

Challenges of bringing WCL ISE technology to icy worlds

- Long cruise times
  - 5 – 10 yrs prior to operation
- Radiation doses
  - 150 krad in the Europa Lander vault
- Smaller packaging of both sensors and the fluidics
  - Original WCL beakers used 25 mL of fluid, analysis of microliter volumes is important for plume capture missions

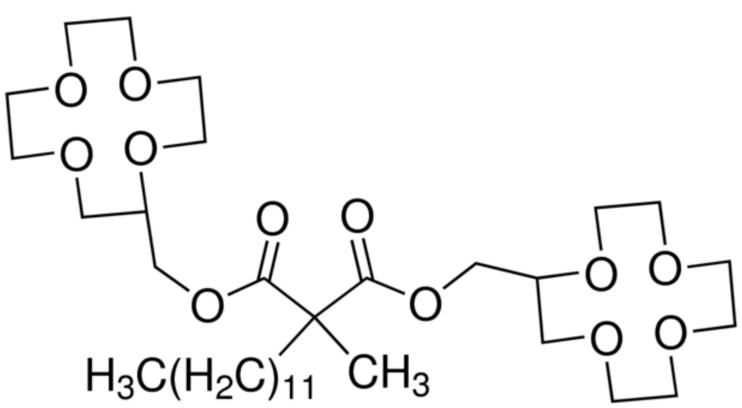
Flight spare and WCL engineering model ISEs work after 10 years of storage!



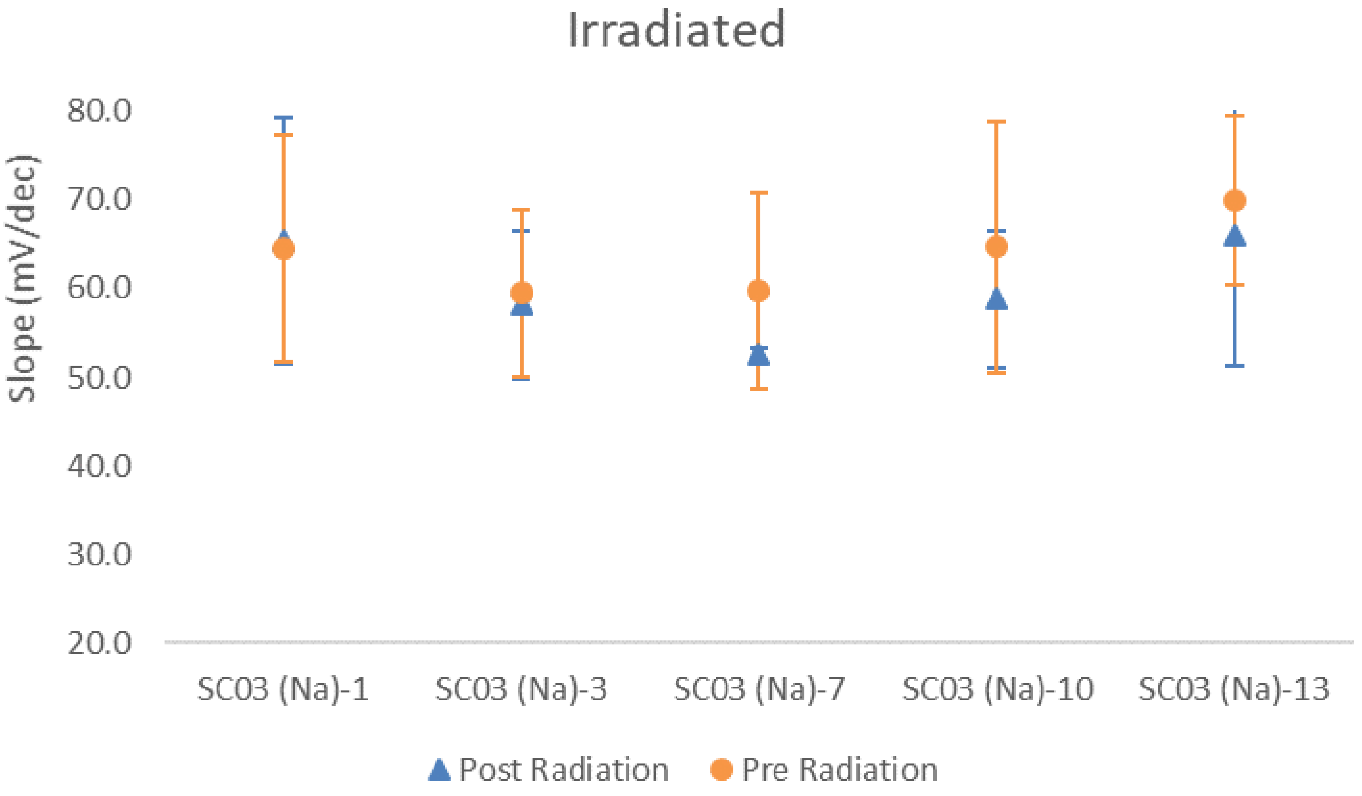


Preliminary results show ISEs survive 300 krad total ionizing dose

Sodium Ionophore VI

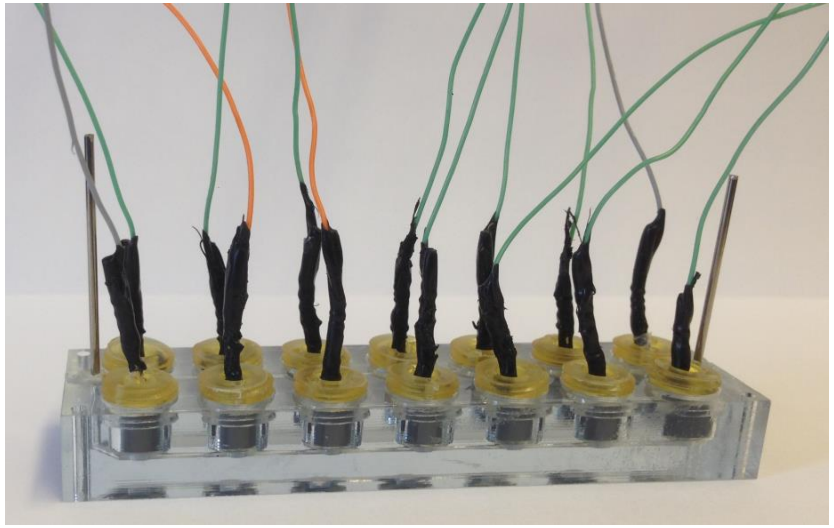


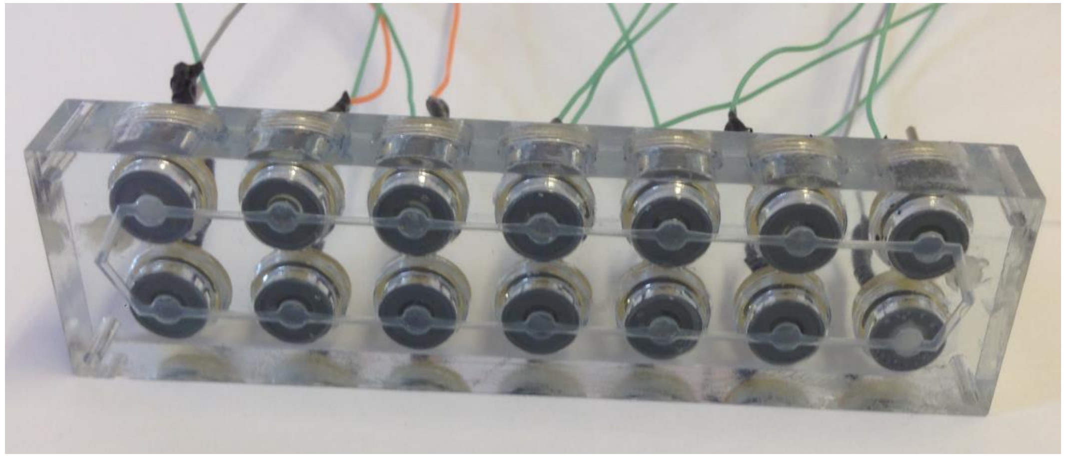
No loss of performance after irradiation

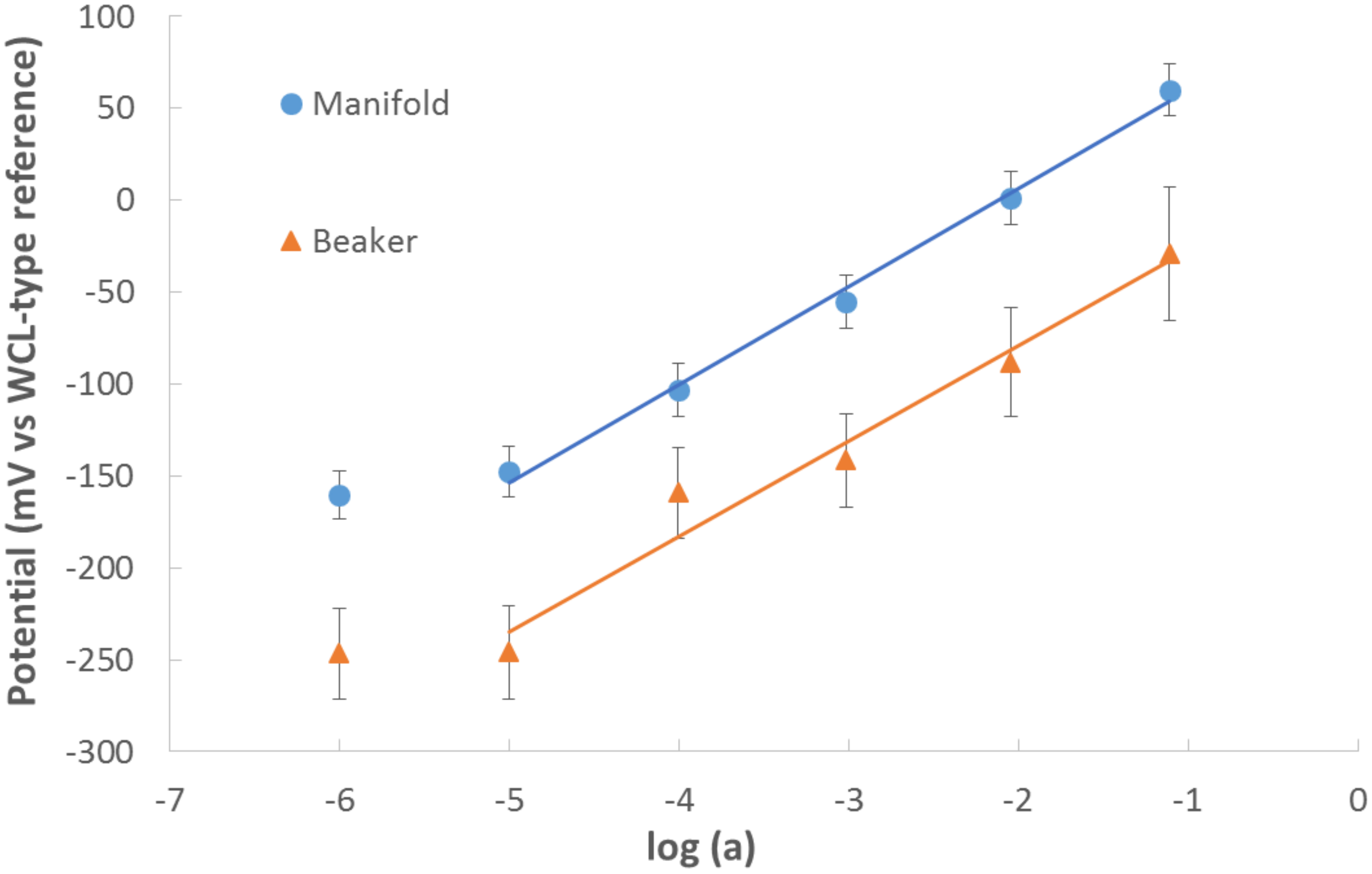


Microfluidic array of ISEs reduce measurement volume to 100 µL

- Channel depth 0.5 mm
- Channel width 1.0 mm
- Total Channel volume 109 µL



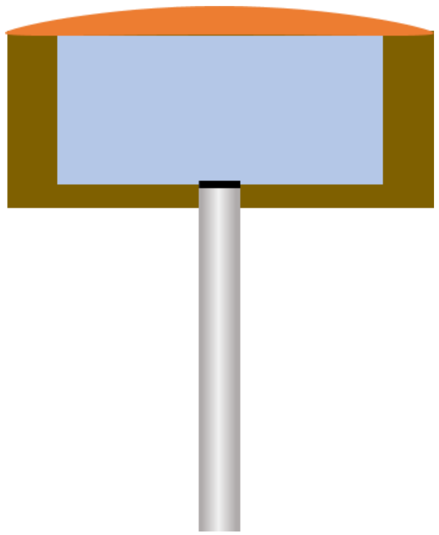




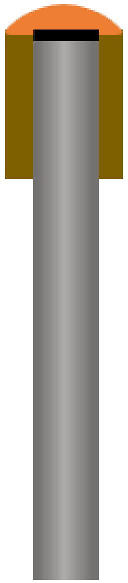
	Beaker	Manifold
Slope	51.8	53.3
RSQ	0.9677	0.9946

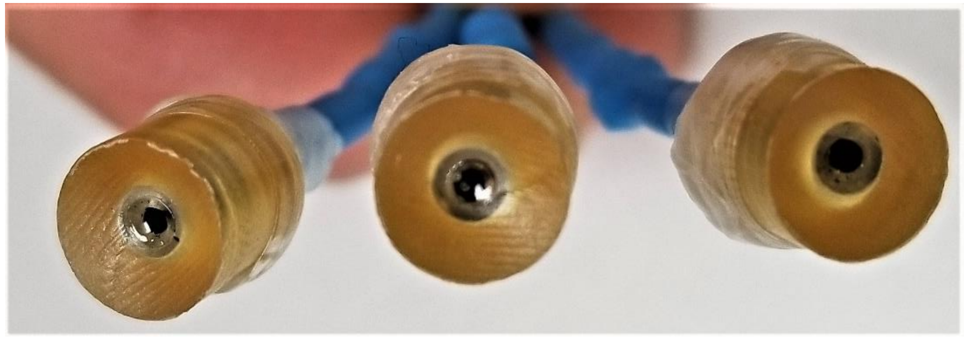
Solid contact ISEs show promise for reducing sensor size while maintaining performance

Heritage WCL design:
6 mm diameter



Next Gen SC design:
2 mm diameter





Conclusions and Acknowledgements

- **ISEs are a proven tool for determining soluble species in planetary samples allowing measurements of habitability and sample context**
- **Tests to date indicate that WCL style ISEs will be compatible with missions to icy worlds**

- Thanks to Mike Hecht, Xiaowen Wen and John Michael Morookian for their advice during this work
- Funding provided by JPL internal Research and Technology Development