USING ION-SELECTIVE OPTRODES TO CHARACTERIZE WATER CHEMISTRY IN EXTREME ENVIRONMENTS. C. G. Thompson[1], P. Sobron[2,3], M. A. Dixon[1], N. Cabrol[2] and the 2013 PLL Team. [1]CESRF University of Guelph, 50 Stone Road, Guelph, Ontario, N1G 2W1, Canada; [2]SETI Institute Carl Sagan Center, 189 Bernardo Ave., Suite 100, Mountain View, CA 94043; [3]MalaUva Labs, 822A Allen Ave, St. Louis MO 630104.

Introduction: Characterizing chemical compounds on the icy surface, and in the lakes of Titan is essential for understanding the astrobiological potential of Titan. Europa has oceans underneath an icy crust that are potentially habitable. Characterizing their chemical composition is therefore a key goal in astrobiology. Future landed missions to these moons will likely require compositional data to be recorded and processed in a reliable, unsupervised, and time and energy efficient way.

There is ample room for developing novel strategies and technologies capable of reliable, robust, affordable measurements. At the University of Guelph we have developed a novel system for multi-ion sensing that includes the use of a spectrometer in tandem with a fiber optic multiplexer that is capable of reading a suite of attached Optrodes, each of them dedicated to a unique ion. A prototype instrument, the Ion-Selective Optrode System (ISOS), was tested in waters of Laguna Negra (Chile) December 12-18 2013. Here we describe the field deployment and report on the successful detection of relevant species using the ISOS: K^+, Na^+, Ca^{2+}, and NO_3^-. Our results demonstrate that Optrodes are a suitable technology to characterize water chemistry in the field and potentially for exploring aqueous environments on other planetary bodies within our solar system.

Background and Objectives: *ISOS Development.* The prototype ISOS is currently under development at the Controlled Environment Systems Research Facility (CESRF), University of Guelph, a lab dedicated to developing Advanced Life Support (ALS) systems for extra-planetary exploration. The prototype was conceived to improve the efficacy of nutrient solution management in plant production systems. The ISOS was designed to collect near-real time data of nutrient ion concentration in hydroponic reservoirs. Ion-Selective Optrode sensors have several advantages over Ion-Selective Electrode sensors: they do not require filling solutions; frequent calibration is not essential; not susceptible to electromagnetic interferences; sensitive components are small, light-weight and inexpensive [1]. The core ISOS components are an LED light source, the Ion-Selective Optrode films, and a spectrometer. Optrode films, designed by collaborators INO (Quebec City, QC), produce a measureable response to ion activities in the form of colour change that can be related to the concentration of a specific ion in solution.

Ion Detection. Presently, the ISOS is capable of ion-selective detection several important ions (K^+, Na^+, Ca^{2+}, NO_3^-); ISOS development is focused on nutrient ions that are physiologically significant to plant production. However, the technology can be tailored to detect virtually any chemical species. Optrodes can also be tailored for specific ranges, and the development of a K^+ and Ca^{2+} sensor for use in hydroponic plant production was documented by Bamsey [2],[3].

Field Deployment. The ISOS was tested in the field in December 2013 during the Planetary Lake Lander (PLL) project field campaign [4]. Our main objective was to determine feasibility of using Optrode technology for science investigations in a field site. The ISOS was tasked with characterizing water chemistry, in-situ, in the context of the development of adaptive science for PLL. The ISOS was reconfigured to accommodate transportation to the remote mountain location and to protect sensitive optical hardware. A design housing all components within a box comparable in size to a desktop computer (32x28x13 cm) was conceived (Fig 1).

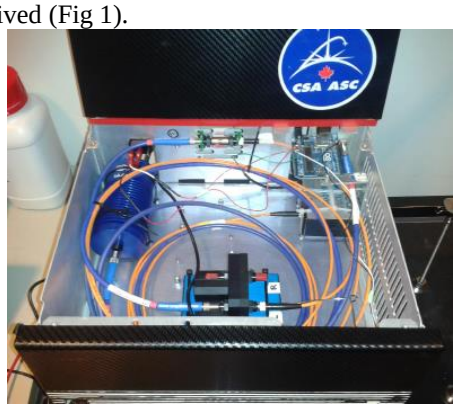

Fig. 1 Hardware box for ISOS prototype showing light source, spectrometer and shutter.

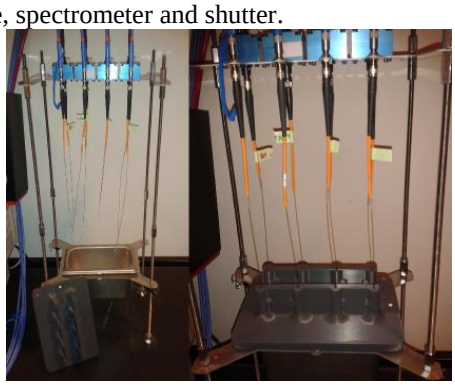

Fig. 2 Fiber tower holding 4 Optrodes. Right image shows fibres covered by light shield.

A light shield was designed to minimize impacts of ambient light on sensor readings and was produced using 3D printing. The light shield was fitted to a sample container mounted within a support tower capable of holding up to 4 Optrode fibres (Fig 2).

Results and Discussion: *Transportation.* The ISOS travelled to the field site via air and truck transportation – all components were in working order upon arrival. Some components had moved around inside the ISOS box yet no damage to optical hardware or fiber connections was observed. The ISOS system will be further ruggedized as the system matures, reducing the risk of transportation damage.

Water Chemistry. Sensors for Ca^{2+}, Na^{+} and NO_3^- were tested in the lake water using samples collected from various locations. The samples were given time to settle to minimize contamination of the Optrodes by suspended solids. The pH of each sample was adjusted using dilute HCl or NaOH to a pH of approximately 7 for all samples (Actual pH values ranged from 6.866-6.989). To demonstrate the function of the ISOS the Optrodes were immersed in 6 different water samples for roughly 5 minutes and readings were taken at 1 minute intervals. In all cases, the sensor response was relatively stable after 30-60 seconds. The process was repeated to ensure that the response was repeatable. Preliminary results shown in Figures 3-4 demonstrate that a sensor response was observed for the Ca^{2+} and Na^{+} Optrodes. The NO_3^- Optrode seemed comparatively less sensitive to changes in sample solution. It is likely that Laguna Negra contains trace amounts of nitrate. Chemical analyses are underway to determine the absolute abundance of ions in several samples from the lake and to evaluate the performance the ISOS.

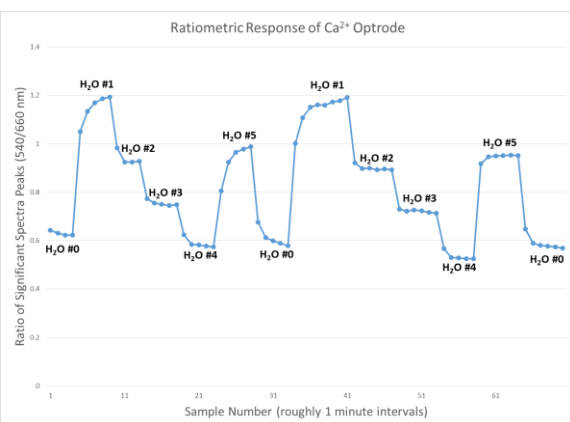

Fig. 3 Data plot illustrating response of Ca2+ Optrode in 6 different water samples collected at Laguna Negra. Sample #0 is pH adjusted distilled water.

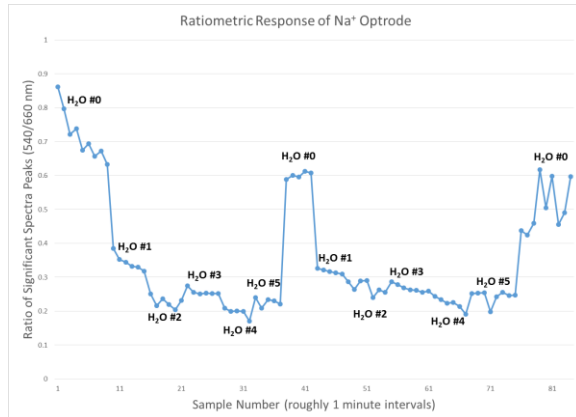

Fig. 4 Data plot illustrating response of Na^{+} Optrode in 6 different water samples collected at Laguna Negra. Sample #0 is pH adjusted distilled water.

Results, although only qualitative so far, demonstrate that the Optrode sensors do perform as expected in the field setting despite the relatively extreme working conditions. Validation of the data collected is pending HPLC analysis of the water samples that were collected. We will report these data at the conference.

Conclusions: The first deployment of the ISOS in the field was a success. The technology demonstrated the ability to selectively detect ions in small concentration within a water source of unknown composition. The field environment imposed some pressure on the ISOS including transportation stress, environmental stress (temperature change, winds), and operational stress (lack of deionized water supply, dust/dirt contamination). The ISOS performed reasonably well in this challenging environment and data collected in the field were of reasonable quality compared to those collected in the lab.

Further development of the ISOS will yield a system that is better suited to field applications considering specifically: miniaturization, optimized packaging, optimized Optrode replacement procedure, optimized sample handling. Ultimately an autonomous ISOS will be developed, well suited for robotic space exploration focused on characterizing extra-terrestrial solution chemistry.

References: [1] Bamsey M. et al. (2012) *Sensors, 12,* 13349-13392. [2] Bamsey M. et al. (2012) *Analytica Chimica Acta,* 737 72–82. [3] Bamsey M. et al. (2014) *Sensors and Actuators B,* 190 61-69. [4] Cabrol N. A. *LPSC 2014 Abstract*.

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