

OXYGEN CONCENTRATION AND COMPOSITION OF MARS ANALOG ACIDIC SALINE ENVIRONMENTS IN WESTERN AUSTRALIA. A. Odenheimer¹, P. Doran², B. E. Schmidt³, J. S. Bowman⁴, S. Som⁵, A. Schartup⁴, E. Ingall⁶, S. Buessecker⁷, E. Quartini³, T. A. Plattner⁶, C. Sephus⁴, J. M. Weber⁸, M. A. Birmingham⁹, L. Fisher⁴, E. Paris⁷, B. Klempay⁴, M. Weng¹⁰, C. Pozarycki⁶, the Esperance Tjaltjraak Native Title Aboriginal Corporation¹¹, M. Towner¹², and the OAST Team. ¹Department of Chemistry & Biochemistry, University of California, Los Angeles, CA (aodenh3@chem.ucla.edu). ²Geology and Geophysics, Louisiana State University (pdoran@lsu.edu). ³Cornell University. ⁴University of California, San Diego. ⁵Blue Marble Space Institute of Science. ⁶Georgia Institute of Technology. ⁷Stanford University. ⁸NASA Jet Propulsion Lab, California Institute of Technology. ⁹University of Kansas. ¹⁰Georgetown University. ¹¹Esperance, WA, Australia. ¹²Curtin University, Perth.

Introduction: The Western Australia Transient Lakes (WATL) are 100s of saline lakes located in the Yilgarn Craton of Western Australia [1]. The Archean Yilgarn craton is approximately the same age as the Noachian and Hesperian rocks on Mars, which make this field site a uniquely suited analog for Mars [1,2]. The WATL were selected for the Oceans Across Space and Time (OAST) study due to the various - physicochemical and biological challenges within these environments that influence the boundary between life and non-life. The WATL are exciting not only because they are chemically and physically diverse, but because they can host complex microbial communities in these extreme settings [3]. OAST seeks to determine habitability in highly saline, low water activity environments on Earth to explore the observable signals of habitability, identify the strategies that life uses to deal with environmental stress, and determine biomarkers that are signals of these conditions. To determine the lower limits of life in these environments, measurements of environmental parameters e.g., pH, temperature, salinity, water activity, ionic strength were taken to establish how they affect life in these extreme settings and how these conditions change over time. This investigation focuses on our 2022 field campaign to the WATL and the chemical measurements taken at each of the lake sites, in order to capture the variable conditions in these lakes over time as they go through wet/dry cycles.

Objective: Our main goals were to characterize the chemical and physical parameters of every site visited in Western Australia and to develop more precise methodology for performing field oxygen measurements. Details of the sampling plan are in [4].

Some compositional constraints have been recorded previously for a subset of these lakes [2]; however, these environments are understudied. In our chemical and physical characterizations, we aimed to measure additional parameters and observe any changes from the last time they were studied, and we wanted very precise measurements for various parameters to support the rest of our team's research interests. The parameters we measured included TDS, pH, and temperature as well as

oxidation-reduction potential (ORP), salinity, dissolved oxygen, density, and water activity.

Field Methods: All physical/chemical measurements were performed during the daytime of from August 4th – 17th, 2022. Measurements were taken with handheld probes to get in-situ data of each lake environment.

pH & temperature: An Onset HOBO MX2501 pH and Temperature Logger was utilized to measure the pH of each lake. The logger was suspended in the lake brine until the pH stayed consistent (± 0.02) for over two minutes. Temperature was recorded from the pH probe after stabilization. The pH probe was tested against calibration solution before leaving for the field and upon returning each day. It was calibrated every 3 days with fresh calibration solution, or sooner when needed.

Oxidation-reduction potential (ORP): A YSI EcoSense ORP15A & Temperature Pen was suspended in brine until it varied less than ± 2 mV for 30 seconds.

Salinity: A salinity estimate was found using a refractometer at each lake site, using the Vee Gee Scientific STX-3 Handheld Refractometer. Due to the fact that some of these lakes were extremely saline, some samples had to be diluted in the field. Later, ion and cation and TDS were measured in the laboratory.

Dissolved Oxygen (logging & Winkler titrations): We had two different methods for measuring dissolved oxygen. The first method was to use the miniDOt Oxygen Logger, which was placed in each lake brine immediately upon arrival. The logger collected data for 30 - 120 minutes for each lake environment. 30 minutes of data collection was chosen from excessive testing. If time permitted, it was left in the brine for 2 hours to observe any changes during our time in the field.

The second method for measuring dissolved oxygen was by using Winkler titrations. For this method, brine was collected in the field at each lake environment with scintillation vials that were rinsed twice with brine from the site and then sealed underwater with no bubbles. After collecting the brine from each site, the samples were then fixed with 0.9mL of previously prepared manganous solution and alkaline-iodine-azide solution.

The rest of this method was finished back in the lab at the end of each day for each site visited that day.

Lab Methods: For measurements performed in the lab, a 50mL falcon tube was filled with brine from each lake site. Lab methods were used to measure the dissolved oxygen, density, water activity, and TDS, along with anions and cations.

Dissolved Oxygen (Winkler titration): Phosphoric acid was added to each scintillation vial collected in the field at each lake site. Six Winkler titrations, using standardized 0.01M sodium thiosulfate as the titrant, were performed for each sample. The first three titrations provided an estimate for the dissolved oxygen value. The final three titrations resulted in an accuracy of 0.001mg/L dissolved oxygen [5].

Density: Density of each lake sample was measured using the Anton Paar DMA 35 Portable Density Meter. In case the sample injection tube was contaminated, an aliquot of sample to be tested was separated from the 50mL falcon tube to prevent cross contamination between samples. The meter was rinsed with DI water three times and emptied until the meter read below 0.005g/cm³ to ensure the meter was free of previous sample.

Water activity: Water activity was measured for each lake site with the AQUALAB 4TE set to record water activity until the value was stable, then retested until three consecutive tests were consistent (± 0.0005). A DI water sample was tested each day to assess if calibration was needed for the probe. Because water activity changes with temperature, the initial temperature of the DI water was used to determine the ambient temperature of the room to calibrate the instrument. The AQUALAB 4TE was cleaned and recalibrated every 5 days or sooner, if needed.

TDS: Values of TDS are most accurate when the measured value for a sample is ≤ 200 mg where a water-trapping crust cannot form when dried [6]. To achieve this, a calculated aliquot of brine from each site was diluted to 250mL. 20mL of this was then taken, passed through a 2.0 μ m filter, dried in an oven at 180 \pm 2 $^{\circ}$ C, and measured with a desired result of 10-200mg of dissolved solids [6]. TDS for the original sample was then calculated. Estimates for the dilution steps were based on the salinity measurements taken in the field. TDS is still being measured at Louisiana State University.

Results: We measured the salinity, pH, temperature, oxidation reduction potential (ORP), density, total dissolved solids, water activity, and dissolved oxygen (DO) of roughly ~40 lakes have the following measured parameters, with the variability outlined in Table 1.

The lakes studied in Western Australia represent an extreme range of values for all parameters measured,

which show how geochemically diverse, complex and variable these lake environments are despite their geographic proximity. Our measured values from the winter season vary drastically from previously recorded measurements; however, previous studies were mainly done in summer [2] in Western Australia.

	pH	ORP (mV)	DO (mg/L)	Salinity (ppt)	Density (g/cm ³)	Temp (°C)	Aw
L o w	2.68	8.2	*0 – 1.108	15	1.0069	9.31	0.7497
H i g h	9.17	469	10.963	360	1.2036	21.3	0.9917

Table 1: Full range of parameters for all sites visited during our fieldwork. *DO reported values from Winkler titrations. 0mg/L reported for hues indiscernible from clear water.

We also found that color perception significantly affects colorimetric methods, such as the Winkler titration. This titration relies heavily on one's ability to perceive very small color changes. For all sites that were studied by our two separate teams at different times, the Team B values were consistently higher than the Team A values for dissolved oxygen. These values generally varied greater than 1mg/L but could vary as much as 3.879mg/L. We are working to extract additional sensor data to complement these field-based data, so it is likely that the true value is somewhere between the presently reported values from each team. Both teams performed the Winkler titrations in the same manner with the same reagents and equipment, leading the only reason for such great differences in values to be our color perception and color difference threshold.

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