METHANE CYCLING IN SMALL, THERMOKARST LAKES IN SOUTHWESTERN GREENLAND AS AN ANALOG FOR EARLY, WET MARS.

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Introduction: Since the putative-discovery of methane in the martian atmosphere in 2003 [1,2,3] there has been debate concerning geochemical or biogeochemical pathways for the origin and destruction of volatitle hydrocarbons on Mars [4]. On Earth, methane emissions are predominantly derived from thermal cracking of ancient organic matter in the deep subsurface or from microbial methanotrophic metabolism in low-salinity aquatic environments such as wetlands and lakes [5,6.7]. Detailed study of methane cycling in thermokarst lakes on the ice-free margin of Greenland provides an appropriate analog for plausible martian ecologies in seasonally ice-covered paleolakes.

We concentrate on a chain of 7 small lakes (<1 km^2), spanning a distance < 6 km along a narrow valley overlying a structural shear zone and extending from the Russell Glacier to the Søndre Strømfjord in southwestern Greenland [Fig. 1]. Bedrock at the study site is composed of ultramafic alkaline dyke swarms with varying amounts of pyroxene, olivine, hornblende and carbonate minerals [8], a mineralogically useful analogue for martian regolith. Due to close proximity we anticipated similar physical parameters and methane concentrations. Here, we describe the preliminary results from two weeks of fieldwork in summer 2011 and four weeks of fieldwork in summer 2012, concentrating on aquatic chemistry combined with methane concentrations and isotopic compostions of methane through the water profile of the lakes.

Figure 1. Lake location map: 1) EVV Upper Lake, 2) EVV Lower Lake, 3) Teardrop Lake, 4) Potentilla Lake, 5) Little Long Lake, 6) North Twin Lake, 7) South Twin Lake.

Site Description: The study area occurs between the airport/village at the head of the Søndre Strømfjord, Kangerlussuaq and the active terminal moraine of the Russell Glacier. The area is characterized by a Low Arctic continental climate [9], with continuous permafrost < 1m below surface and low precipitation (< 150 mm yr^{-1}). The mean annual air temperature is -6°C, with peaks of +20°C in June to early August when mean temperatures are over +8°C. The lakes are ice-covered from mid-September to mid-June. Due to minimal precipitation, lakes are supplied with water mainly through contributions from the melting snowpack. Groundwater seepage is probably very limited due to a negative precipitation-evaporation balance and the presence of permafrost [10].

Methods: Samples were collected from the center of each lake off the side of a boat in Summer 2012. Physiochemical parameters of temperature, pH, dissolved oxygen, oxidation/reduction potential, and conductivity were measured using a YSI Data Sonde deployed at 0.5 m depth increments. Additional water was collected with Kemmerer vertical sampler and stored frozen in Nalgene bottles for further analysis.

Methane. Dissolved methane was stripped in the field using an Erlenmeyer flask engineered with a 3-way luerlock inlet and 3-way luerlock valve attached to the stopper. For each 500 mL of water, the valves are closed and flask is shaken vigorously for 1 minute to release gas. Gas was displaced into an attached Tedlar bag by injecting water through the syringe. Ebullition gas samples were collected from littoral sediments using a 28 cm diameter plastic funnel with a gas-tight sampling tube and 3-way luerlock valve attached to the neck. Gas was collected into an attached Tedlar bag.

Methane concentrations and carbon isotopes were measured using a Los Gatos Research (LGR) Methane Carbon Isotope Analyzer (MCIA) at the field station in Kangerlussuaq, Greenland. The LGR MCIA measures the two stable isotopes of carbon (^{12}C and ^{13}C) in methane for both continuous flow and discrete gaseous samples without sample preparation. This benchtop model uses LGR's patented off-axis ICOS technology, a cavity enhanced absorption technique. All samples were processed within 24 hours of collection.

Aqueous Chemistry: All lakes have similar stratified thermal properties, but there are substantial variations in the aqueous chemistry of the lakes. Hypolimnions range from pH 6.5 to 9.5; Teardrop is buffered by bicarbonate with limited vertical variation in pH between 9.5 and 9.1, while the pH in adjacent Potentilla Lake (Fig. 1) varies vertically from pH 9.4 to 7.2. Conductivity varies markedly from lake to lake, ranging from saline (>800 µS cm^{-1}) to dilute (<500 µS cm^{-1}). Variability is not dependent on distance; nearly an order of magnitude difference in conductivity (2,900 to 250 µS cm^{-1}) is observed between North

Twin Lake and South Twin Lake, despite being separated by only 0.25 km (Fig. 1).

Methane: Methane concentrations range from 34 to 15,000 ppm [Fig. 2]. Concentrations in each lake are highest in the hypolimnion, and decrease up the water column. Values of methane $\delta^{13}C$ vary between the lakes, with averages ranging from -30‰ to -70‰.

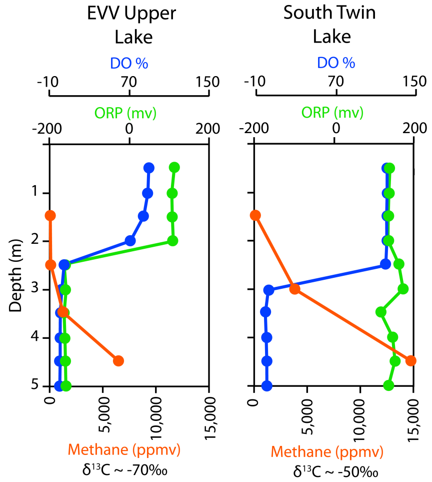

Figure 2. Methane, dissolved oxygen, oxidation/reduction potential (ORP) for EVV Upper Lake and South Twin Lake. Values of $\delta^{13}C$ are averages over the entire water column.

Methane ebullition from near-shore sediments was only collected from Teardrop Lake, Potentilla Lake and South Twin Lake. Concentrations range from 320,000 to 434,000 ppmv. Values of $\delta^{13}C$ range from -46 to -53‰ respectively.

Discussion: Due to thermal stratification, methane concentrations are controlled by the thermocline and oxycline in each lake. As a result of diffusive export from anoxic sediment, methane enters the water column, where there is a buildup in the anoxic hypolimnion resulting in storage. As methane reaches oxic water in the metalimnion, a large proportion is likely oxidized by methane-oxidizing bacteria, resulting in the sharp decrease in concentration at depths that correspond with increases in dissolved oxygen and oxidation/reduction potential.

Methane concentrations in the epilimnion ranged from 30-100 ppm. This represents the concentration of methane that escapes oxidation and may contribute to ebullitive or diffusive flux. The diffusive flux depends on the difference in methane concentration between the water and atmosphere and the physical rate of exchange due to piston velocity [6].

Values of $\delta^{13}C$ for dissolved methane from EVV Upper Lake, Teardrop Lake, Potentilla Lake and Teardrop Lake were <-45‰, suggesting a microbial source [11]. Without measured values of $\delta D\text{-}CH_4$, the production pathway cannot be constrained. In EVV Lower Lake, values of $\delta^{13}C$ were > -40‰, suggesting either a distinctly different methane source or more methane oxidation.

The concentrations of methane determined by ebullition from oxic sediments is nearly 30 times that of methane in gas stripped from hypolimnions, indicating an important potential flux. Values of $\delta^{13}C$ were <-45‰, suggesting a biological source [11]. Measurements from more lakes and from anoxic sediments are needed to further understand the potential for methane ebullition in this ecosystem.

Plant-mediated emission from emergent and submergent vegetation in the littoral zone is dependent on methane production and oxidation in the sediments and the vegetation characteristics. More information on these processes is needed to understand the role of littoral plants to methane cycling in these thermokarst lakes.

Conclusions: Similarly stratified thermal properties are observed between small lakes at a study site on the ice-free margin of southwestern Greenland. Despite their close proximity, there are substantial variations in the aqueous chemistry of these lakes with no unifying trends observed between depth, surface area, and aquatic chemistry. Dissolved methane concentrations reflect the positions of the thermocline and oxycline in each lake, however variations are observed in CH_4 concentration and $\delta^{13}C\text{-}CH_4$ between lakes. In the absence of throughgoing drainage systems, small lakes embedded in thermokarst operate independently despite close proximity. The physiochemical diversity observed is likely due to ecological and hydrogeochemical factors such as differences in bedrock and vegetation. Further work is needed to identify factors influencing sources and sinks of methane for each lake.

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