TRACKING ORGANIC MOLECULES IN CRATER MELT PONDS ON TITAN. J.E. Hedgepeth[1]J. Buffo[2], C.D. Neish[1], B.E. Schmidt[3], C. Chivers[3], [1]University of Western Ontario (1151 Richmond St, London, ON N6A 3K7, Canada; jhedgepe@uwo.ca), [2]Dartmouth College (Hanover, NH 03755), [3]Georgia Institute of Technology (North Ave NW, Atlanta, GA 30332)

Introduction: Saturn's moon Titan is unique among the natural satellites because it has a thick atmosphere composed mostly of nitrogen and low amounts of methane. Solar radiation fuels the dissociation and ionization of these molecules, and over time heavy organics form [1]. These organics cover the surface of Titan in the form of aerosols, global sand dunes and rivers, lakes and seas of liquid hydrocarbons [2]. The interaction of these organics with the surface creates a diverse landscape uncannily similar to Earth's, both geologically and, in the case of the early Earth, chemically [3].

This is the motivation for the new mission to Titan, Dragonfly, recently selected for NASA's New Frontiers program [4]. The mission will send a quadcopter to Titan's surface to gain an unprecedented look at the surface with a focus on studying the rich organic environment. These heavy organics are considered an important component in the origin of life as they form biomolecules, such as amino acids, when mixed with water, and Dragonfly intends to sample these molecules [3, 4]. While liquid water is rare on Titan's 94 K surface, there are instances where it is thought to have existed, if only temporarily [5, 6].

On Titan, the two best candidates for liquid water are cryovolcanic flows and melt formed in fresh impact craters. Cryovolcanic flows are thought to be rare, and even those that do form are likely to expel cold ammonia rich water from Titan's subsurface ocean [5, 6]. Temperature is key because prebiotic chemical reactions require time and energy. Impact craters are likely to be more conducive to the origin of life than cryovolcanic flows, because melt ponds can be thicker (possibly 100s of meters thick) and warmer (273 K and up) [7]. This leads to a longer and more energetic period over which this chemistry can evolve (while the water remains liquid).

Dragonfly intends to target a relatively fresh crater during its mission [4]. It may be possible to use methane river valleys in this crater to access subsurface, frozen melt [6]. However, no work has been done to constrain where the products of this prebiotic chemistry will be embedded into the ice as the melt pond freezes. In order for Dragonfly to adequately sample the melt for prebiotic products, the team has to understand the geologic history of the water-organic mixture. That is to say, we need to constrain how and when the organics were "fossilized" within the ice.

On Earth, most impurities are rejected as ice freezes [8], but the physics that controls how much is rejected varies by thermal gradient, concentration, and chemistry [9, 10]. In this work, we need to (a) constrain how much of the impurities become entrapped in the ice versus rejected into the remaining liquid fraction, for (b) the type of organics observed on Titan under the conditions observed in fresh impact crater melts. The purpose of this project is to use the planetary ice model SlushFund2.0-v2 (SF2) [11] to track the concentrations of molecular impurities, both within the ice and the residual melt, as the melt pond refreezes.

Model: SF2 is a multiphase reactive transport model of planetary ices based on terrestrial sea ice dynamics [9]. It is a 1D model that tracks the salinity, temperature, and liquid fraction at the ice-water boundary. As water freezes, impurities are concentrated within the residual liquid fraction (pore space) of the two-phase interfacial layer. In sea ice, this translates to pockets and veins of concentrated brines [12]. The model utilizes the mushy layer theory of Feltham et al. [13]. Here, "mushy" refers to multiple components or phases existing in a system, and it allows for different regions (ice, water, brine) to be described with the same set of equations.

Buffo et al. [10] uses the enthalpy method developed by Huber et al. [14] to iteratively calculate the liquid fraction of each cell. Finally, a density difference is created by the concentration gradient, so the SF2 [11] accounts for it by using the approach of Griewank and Notz's 1D model of gravity drainage [15].

Methods: The 1D model tracks the temperature and chemistry in finite increments throughout the depth of a melt pond by focusing on the upper most meter of the liquid section at the mushy water-ice layer. We replace the salt impurity with organic HCN because of its prominence on Titan [16] and its well-studied chemistry [17]. We track the model for concentrations of up to 25% (250 ppt) at depths of up to 200 m [7].

As each increment (1 cm) in this upper meter freezes, the ice reaches a critical porosity that is estimated from terrestrial ice studies [18]. At this point, the ice is assumed to be frozen enough such that all the liquid brine, trapped in pockets and veins, is closed off from the liquid pocket. The impurities become fixed in the ice, and the 1 m mushy layer moves down to the next increment of the melt pond. Buffo et al. [11] used the physics that governs the model to develop analytical solutions for the concentration of impurities frozen into the ice. We use the same analytical solutions to expedite the modeling process by solving for enough sections of depth (and thermal gradients) with the 1D model to fit an analytical solution to the entire depth profile (Figure 1).

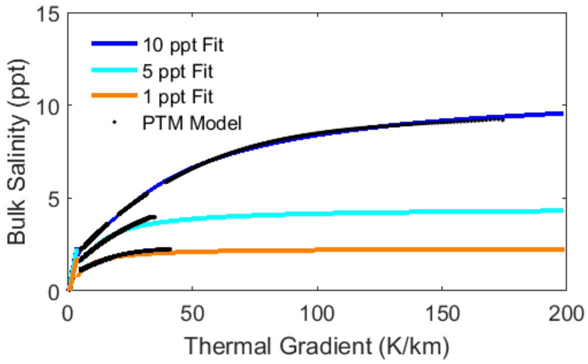

Figure 1. Concentration of HCN (ppt) in the ice under Titan conditions for initial concentrations of 1 ppt (0.1%), 5 ppt (0.5%), and 10 ppt (1%) at different thermal gradients. The SF2 model results are shown with black points, and the analytical fits are shown with solid lines of blue (10 ppt), light blue (5 ppt), and orange (1 ppt).

Discussion and Results: Basic fluid dynamics offers a guide for how impurities are transported within a fluid [19]. In sea ice, the removal of salt is gravity driven because of its buoyancy differences [10, 11], so the specific chemistry of the impurity is a major factor in how the system operates. HCN is different than salt because it is lighter than water and ice [16]. Therefore, the lower buoyancy will invert the system such that impurities are removed at the lower boundary, while at the top, gravity does not drive the removal of impurities. Similar scenarios have been studied in terrestrial lavas where less dense melt becomes suspended in a lava chamber with denser melts settling on the bottom [20]. We propose that HCN in a Titan melt pond would follow the same pattern as less dense impurities in terrestrial lavas because of its buoyancy relationship to water and ice.

With this understanding, we can begin to develop a more complete picture of our system (Figure 2). A melt pond will freeze from all directions, removing impurities at the bottom layer while trapping impurities at the top. A key feature of this system is that it is a closed finite body of water. SF2 assumes the mushy layer is atop an infinite ocean because the rejected impurities will never significantly affect the bulk concentration of the ocean, but the bulk concentration of a melt pond will become progressively more concentrated.

Therefore, we use the SF2 to model melt ponds at a range of initial bulk concentrations and interpolate between each to create a reference for a simple mass balance analysis assuming a melt pond of a given size. Figure 1 shows the final concentration of HCN for a given thermal gradient within a range of initial concentrations. This allows us to quantify how much will freeze into the ice in a closed system (Figure 2). The best samples will likely be near the middle (where more time would have elapsed for chemical reactions), but we would expect to find some HCN near the surface if it was a pure HCN-water mixture. However, the same may not be true for denser molecules.

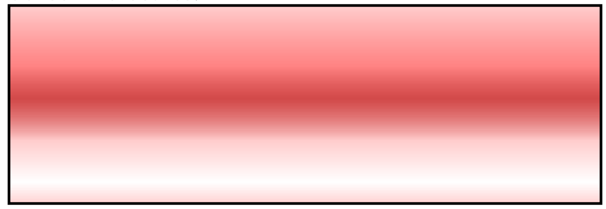

Figure 2. A hypothetical melt-pond of an HCN-water mixture after freezing, shown in side view assuming an approximately cylyndrical shape. Concentration is shown as shades of red, darker being more concentrated. White is pure ice. The impurities will remain in the ice at the top but be (mostly) rejected at the bottom. Rejection at the bottom increases bulk cocentration (and the concentration frozen into the upper ice) until the layers meet and concentrate in the center.

Future Work: Buoyancy is likely the most significant difference between HCN and salt. We choose to use HCN as a starting point, but more work is still needed to understand how other chemistries will act in this type of system. Thus, in future work we plan to test an organic that is denser than water. Finally, we plan to consider bulk chemistries that are likely to be found on Titan (rather than a mixture of water with one organic). The system becomes more complicated as we reach more complex chemistries because less is known about their chemical properties in water. Ideally, future work will include experimental freezing of melt under the same conditions (chemistry, temperatures and thermal gradients), to offer a way of benchmarking our results.

Acknowledgments: J.H. would like to thank the Technologies for Exo-Planetary Science (TEPS) NSERC CREATE program for funding that supported this work.

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